

**Rational Design and Synthesis of Advanced
Nanocrystals with Enhanced Electrocatalytic
Activities for Water Splitting**

Xuesong Zhang

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Rational Design and Synthesis of Advanced Nanocrystals with Enhanced Electrocatalytic Activities for Water Splitting

Doctoral Thesis in Materials Science

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Dr. Pablo Guardia Girós, tenured scientist at CSIC in the Institute of Materials Science of Barcelona (ICMAB-CSIC), and Prof. Anna Roig Serra, leader of the Group of Nanoparticles and Nanocomposites at ICMAB-CSIC, hereby certify that Xuesong Zhang, holder of a Master's degree in Chemical Engineering, has carried out the research work entitled:

"Rational Design and Synthesis of Advanced Nanocrystals with Enhanced Electrocatalytic Activities for Water Splitting"

This work has been conducted within the framework of the Doctoral Program in Materials Science of the Department of Chemistry at the Autonomous University of Barcelona.

To serve as proof thereof, this certificate is hereby signed.

Dr. Pablo Guardia Girós

Prof. Anna Roig Serra

Campus de la UAB, Bellaterra, 14 of July of 2025

“读万卷书，行万里路”

谨以此句致敬我最后的学生时代

"To those I hold dear

whose love has warmed my heart

and whose presence has shaped my journey

this work is for you."

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Acronyms

AC	Alternating Current
AEM	Adsorbate Evolution Mechanism
AEMHE	Anion Exchange Membrane Hybrid Electrolysis
AEMSE	Anion Exchange Membrane Seawater Electrolyzer
AEMWE	Anion Exchange Membrane Water Electrolyzer
Ag/AgCl	Silver/Silver Chloride Reference Electrode
AI	Artificial Intelligence
AOR	Alcohol Oxidation Reaction
ATR	Attenuated Total Reflectance
AWE	Alkaline Water Electrolyzers
CA	Chronoamperometry
CB	Carbon Black (Vulcan CX-72)
CC	Carbon Cloth
C_{dl}	Electrochemical Double-layer Capacitance
CE	Counter Electrode
CNTs	Carbon Nanotubes
CO ₂ RR	Carbon Dioxide Reduction Reaction
CP	Chronopotentiometry
CPE	Constant Phase Element
CPET	Concerted Proton-Electron Transfer
C_s	General Specific Capacitance
CV	Cyclic Voltammetry
DEMS	Differential Electrochemical Mass Spectrometry
DFT	Density Functional Theory
DMSM	Dual-Metal Site Mechanisms
E	Applied Potential
E_0	the Theoretical Equilibrium Potential
ECSA	Electrochemical Active Surface Area
EDX	Energy Dispersive X-ray Spectroscopy
EELS	Electron Energy Loss Spectroscopy
EG	Ethylene Glycol
EIS	Electrochemical Impedance Spectra
EOR	Ethanol Oxidation Reaction
EPR	Electron Paramagnetic Resonance
EU	European Union

F	Faradic Constant
FE	Faradic Efficiency
FT-IR	Fourier Transform Infrared Spectroscopy
GGA	Generalized Gradient Approximation
HAADF-STEM	High-angle Annular Dark-field Scanning Transmission Electron Microscope
H _{ads}	Adsorbed Hydrogen Atoms
HEAs	High-entropy Alloys
HER	Hydrogen Evolution Reaction
Hg/HgO	Mercury/Mercury Oxide Reference Electrode
HR-STEM	High-Resolution Scanning Transmission Electron Microscope
H _{UPD}	Hydrogen Underpotential Deposition
ICP-OES	Inductively Coupled Plasma Atomic Emission Spectroscopy
IEA	International Energy Agency
<i>j</i>	Current Density
LDH	Layered Double Hydroxides
LOM	Lattice Oxygen Mechanism
LSPR	Local Surface Plasmon Resonance
LSV	Liner Sweep Voltammetry
MA	Mass Activity
M-B	Metal-boron bonding
MEAs	Membrane Electrode Assemblies
ML	Machine Learning
M-O	Metal-oxygen bonding
MOR	Methanol Oxidation Reaction
MQ-H ₂ O	Milli-Q Water
MW	Microwave
M _w	Molecular Weight
N ₂ RR	Nitrogen Reduction Reaction
NCs	Nanocrystals
NF	Nickel Foam
NMR	Nuclear Magnetic Resonance
O-B	Oxygen-boron bonding
OER	Oxygen Evolution Reaction
O-O	Oxygen-oxygen bonding
ORR	Oxygen Reduction Reaction
O _v	Oxygen Vacancies
OVSM	Oxygen Vacancy Site Mechanisms

PAW	Projector Augmented Wave
PBE	Perdew-Burke-Ernzerhof
PBS	Potassium Phosphate-buffered Saline
PDOS	Projected Density of States
PEMWE	Proton Exchange Membrane Water Electrolyzers
Pt/C	Commercial Platinum Carbon
PVP	Polyvinylpyrrolidone
R_{ct}	the Charge Transfer Resistance
RDS	Rate-determining Step
RE	Reference Electrode
RHE	Reversible Hydrogen Electrode
R_s	the Internal Resistance
S	Selectivity
SACs	Single-atom Catalysts
SCF	Self-consistent Field
SEM	Scanning Electron Microscopy
SMR	Steam Methane Reforming
SMSM	Single-metal Site Mechanisms
SOEC	Solid Oxide Electrolyzers
STEM	Scanning Transmission Electron Microscopy
TDOS	Total Density of States
TEM	Transmission Electron Microscope
TMAOH	Tetramethylammonium Hydroxide Solution
TMOs	Transition Metal Oxides
TOF	Turnover Frequency
UV-vis	Ultraviolet-visible Spectra
VASP	Vienna Ab Initio Simulation Package
WE	Working Electrode
XAS	X-ray Absorption Spectroscopy
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
η	Overpotential

Abstract

The global reliance on fossil fuels has triggered both an energy and environmental crises, necessitating an urgent transition to a more sustainable society. As a carbon-neutral energy carrier with high gravimetric ($140 \text{ MJ}\cdot\text{kg}^{-1}$) and volumetric ($8.5 \text{ MJ}\cdot\text{L}^{-1}$) energy density, hydrogen offers significant promise for decarbonization across multiple sectors. Among various production routes, water electrolysis, powered by renewable or low-carbon electricity, has emerged as the most viable approach for large-scale green hydrogen generation. However, the widespread deployment of this technology is constrained by the high cost and limited availability of non-noble metal electrocatalysts, with Pt for the hydrogen evolution reaction (HER) and Ir/Ru-based materials for the oxygen evolution reaction (OER) benchmark catalyst.

This thesis addresses these challenges through the rational design and synthesis of nanostructured catalysts aimed at enhancing both cathodic and anodic activities, while minimizing or replacing the use of noble metals with more abundant alternatives. For instance, replacing Pt for the HER remains a significant challenge, as it exhibits the lowest overpotential along with excellent long-term stability. Instead of full substitution, reducing Pt content while maintaining or enhancing catalytic performance is a promising strategy to meet the growing demand for hydrogen. **Chapter 2** presents a microwave (MW)-assisted colloidal synthesis of Au@Pt core-shell nanocrystals. Chlorine incorporation is used to modulate reaction kinetics, with the Au core acting as an electron-transfer accelerator and the Pt-rich shell maximizing active site exposure. This architecture substantially enhances HER activity in acidic media while reducing Pt loading.

In the context of overall water splitting, the energy efficiency and reaction kinetics are strongly hindered by the sluggish OER, which severely compromises the scalability of hydrogen production. Despite intensive efforts to discover alternative materials, noble

metal oxides such as RuO_2 and IrO_2 remain the benchmark materials for the OER. Furthermore, most catalysts exhibit poor stability under harsh environments, such as seawater, which restricts hydrogen production to freshwater, a resource that is becoming increasingly scarce. **Chapter 3** addresses this limitation by developing boron- and aluminum-doped NiFe layered double hydroxide (B,Al-NiFe LDH) nanosheets via hydrothermal synthesis. Dopant-induced electronic modulation enhances the lattice oxygen mechanism (LOM), leading to improved OER performance. Density functional theory (DFT) calculations further elucidate the reaction pathway. Notably, the incorporation of Al also contributes to improved activity and stability under seawater electrolysis conditions.

Finally, the kinetic and thermodynamic limitations imposed by the OER can be bypassed by replacing it with more favorable oxidation reactions. In recent years, the oxidation of small organic molecules, such as methanol and ethanol (MOR and EOR), has gained attention as a promising alternative. **Chapter 4** explores the design and synthesis of novel electrocatalysts for efficient MOR and EOR. Cu@CoO core-shell nanocrystals, synthesized via a MW-assisted method, demonstrate superior activity in methanol and ethanol oxidation, yielding formic and acetic acid as primary products, respectively, thereby adding value to the electrolysis process. Remarkably, the efficiencies measured for these catalysts in the EOR clearly outperform those of current state-of-the-art electrocatalysts. This is particularly noteworthy given the potential to produce ethanol from sustainable resources such as agricultural waste. Collectively, this work contributes both to the fundamental understanding and the development of cost-effective, high-performance catalysts for sustainable hydrogen production.

Resumen

La dependencia global de los combustibles fósiles ha provocado una crisis energética y medioambiental, haciendo necesaria una transición hacia una sociedad más sostenible. Como portador de energía neutro en carbono, y con una alta densidad energética gravimétrica ($140 \text{ MJ}\cdot\text{kg}^{-1}$) y volumétrica ($8.5 \text{ MJ}\cdot\text{L}^{-1}$), el hidrógeno ofrece la descarbonización en múltiples sectores. Entre las distintas vías de producción, la electrólisis del agua alimentada por electricidad renovable, o de bajas emisiones, emerge como uno de los enfoques más viables para la generación de hidrógeno verde a gran escala. Sin embargo, la escasa alternativa a electrocatalizadores basados en metales nobles como por ejemplo el platino (Pt) para la reacción de evolución de hidrógeno (HER) y materiales basados en iridio (Ir) o rutenio (Ru) para la reacción de evolución de oxígeno (OER), limita su aplicación.

Esta tesis aborda dichos desafíos mediante el diseño y la síntesis de catalizadores nanoestructurados orientados a mejorar tanto las actividades catódicas como anódicas, al tiempo que se reduce o sustituye el uso de metales nobles. Por ejemplo, sustituir el Pt en la HER representa un reto considerable ya que este exhibe el menor sobrepotencial junto con una excelente estabilidad. Una estrategia prometedora consiste en reducir el contenido de Pt manteniendo o mejorando el rendimiento catalítico, lo que permitiría satisfacer la creciente demanda de hidrógeno. El **Capítulo 2** de esta tesis presenta la síntesis coloidal asistida por microondas (MW) de nanocristales con una estructura tipo núcleo-corteza Au@Pt. La incorporación de cloro en la síntesis permite modular la cinética de reacción, utilizando el núcleo de oro para promover la transferencia de electrones a la corteza y enriqueciendo la superficie con átomos de platino. Esta arquitectura mejora significativamente la actividad HER en medio ácido, a la vez que reduce la cantidad de Pt utilizada.

En el contexto de la electrólisis global del agua, la eficiencia energética y la cinética

de la reacción se ven fuertemente limitadas por la lentitud de la OER, lo cual compromete seriamente la escalabilidad de la producción de hidrógeno. A pesar de los esfuerzos intensivos por encontrar materiales alternativos, los óxidos de metales nobles como RuO_2 e IrO_2 siguen siendo los materiales de referencia para la OER. Además, la mayoría de los catalizadores presentan escasa estabilidad en condiciones agresivas, como el agua de mar, lo que restringe la producción de hidrógeno al uso de agua dulce, un recurso cada vez más escaso. El **Capítulo 3** aborda esta limitación mediante el desarrollo de nanoláminas de hidróxidos dobles laminares (LDH) de NiFe dopados con boro y aluminio (B,Al-NiFe LDH). La modulación electrónica inducida por los dopantes favorece el mecanismo mediado por oxígenos de la red (o estructura, LOM), mejorando el rendimiento catalítico de la OER. Cálculos basados en la teoría del funcional de la densidad (DFT) permiten dilucidar la ruta de reacción. Cabe destacar que la incorporación de Al también contribuye a una mayor estabilidad incluso en electrólisis con agua de mar.

Finalmente, las limitaciones cinéticas y termodinámicas impuestas por la OER pueden superarse sustituyendo esta reacción por otras basadas en la oxidación de moléculas más favorables. En los últimos años, la oxidación de pequeñas moléculas orgánicas como el metanol o el etanol (MOR y EOR, respectivamente) ha ganado atención como alternativa prometedora a la OER. El **Capítulo 4** explora este concepto diseñando y sintetizando nuevos electrocatalizadores para MOR y EOR. Los nanocristales con una estructura tipo núcleo-corteza de cobre y cobalto (Cu@CoO), se sintetizaron mediante un método asistido por microondas, muestran una actividad superior en la oxidación de metanol y etanol, generando como productos principales ácido fórmico y ácido acético, respectivamente, lo que aporta valor añadido al proceso de electrólisis. De forma notable, las eficiencias medidas para estos catalizadores en la EOR superan claramente a las de los electrocatalizadores más avanzados disponibles actualmente. Esto resulta particularmente relevante considerando el potencial de producir etanol a partir de recursos sostenibles como los residuos agrícolas.

En conjunto, este trabajo contribuye tanto a la comprensión fundamental como al desarrollo práctico de catalizadores rentables y de alto rendimiento para una producción sostenible de hidrógeno.

Resum

La dependència global dels combustibles fòssils ha provocat una crisi energètica i mediambiental, fent necessària una transició cap a una societat més sostenible. Com a portador d'energia neutre en carboni, i amb una elevada densitat energètica gravimètrica ($140 \text{ MJ}\cdot\text{kg}^{-1}$) i volumètrica ($8,5 \text{ MJ}\cdot\text{L}^{-1}$), l'hidrogen ofereix grans possibilitats per a la descarbonització de múltiples sectors. Entre les diverses vies de producció, l'electròlisi de l'aigua alimentada per electricitat renovable o de baixes emissions emergeix com un dels enfocaments més viables per a la generació d'hidrogen verd a gran escala. No obstant això, el desplegament generalitzat d'aquesta tecnologia es veu limitat per l'escassa disponibilitat d'alternatives als electrocatalitzadors basats en metalls nobles; com ara el platí (Pt) per a la reacció d'evolució d'hidrogen (HER) i els materials basats en iridi (Ir) o ruteni (Ru) per a la reacció d'evolució d'oxigen (OER).

Aquesta tesi aborda aquests desafiaments mitjançant el disseny racional i la síntesi de catalitzadors nanoestructurats orientats a millorar tant les activitats catòdiques com anòdiques, alhora que es redueix o substitueix l'ús de metalls nobles per alternatives més abundants. Per exemple, substituir el platí en la HER representa un repte considerable, ja que presenta el menor sobrepotencial juntament amb una excel·lent estabilitat. En lloc d'una substitució total, una estratègia prometedora consisteix a reduir el contingut de Pt mantenint o millorant el rendiment catalític. El **Capítol 2** d'aquesta tesi presenta una síntesi col·loïdal assistida per microones (MW) de nanocristalls amb una estructura tipus nucli-còrtex Au@Pt. La incorporació de clor durant la síntesi permet modular la cinètica de la reacció, utilitzant el nucli d'or per promoure la transferència d'electrons cap a la superfície enriquida amb àtoms de Pt. Aquesta arquitectura millora significativament l'activitat HER en medi àcid, tot reduint la quantitat de Pt necessària.

En el context de l'electròlisi global de l'aigua, l'eficiència energètica i la cinètica de la reacció es veuen fortament limitades per la lentitud de la OER, fet que compromet seriosament l'escalabilitat de la producció d'hidrogen. Tot i els intensos esforços per trobar materials alternatius, els òxids de metalls nobles com RuO_2 i IrO_2 continuen essent els materials de referència per a la OER. A més, la majoria dels catalitzadors mostren escassa estabilitat en entorns agressius, com ara l'aigua de mar, cosa que restringeix la producció d'hidrogen a l'ús d'aigua dolça, un recurs cada cop més escàs. El **Capítol 3** aborda aquesta limitació mitjançant el desenvolupament de nanolàmines d'hidròxids dobles laminars (LDH) de NiFe dopats amb bor i alumini (B,Al-NiFe LDH). La modulació electrònica induïda pels dopants afavoreix el mecanisme basat en l'oxigen de xarxa (LOM), millorant el rendiment catalític de la OER. Càlculs basats en la teoria del funcional de la densitat (DFT) permeten dilucidar la ruta de reacció. Cal destacar que la incorporació d'Al també contribueix a una major estabilitat, fins i tot en condicions d'electròlisi amb aigua de mar.

Finalment, les limitacions cinètiques i termodinàmiques imposades per la OER poden ser superades substituint aquesta reacció per d'altres basades en l'oxidació de molècules més favorables. En els darrers anys, l'oxidació de petites molècules orgàniques com el metanol o l'etanol (MOR i EOR, respectivament) ha despertat interès com a alternativa prometedora a la OER. El **Capítol 4** explora aquest concepte mitjançant el disseny i síntesi de nous electrocatalitzadors per a MOR i EOR. Els nanocristalls amb estructura tipus nucli-còrtex de coure i cobalt (Cu@CoO), sintetitzats mitjançant un mètode assistit per microones, mostren una activitat superior en l'oxidació de metanol i etanol, generant com a productes principals àcid fòrmic i àcid acètic, respectivament, fet que aporta un valor afegit al procés d'electròlisi. De manera notable, les eficiències mesurades per a aquests catalitzadors en l'EOR superen clarament les dels electrocatalitzadors més avançats disponibles actualment. Això és especialment rellevant si es considera el potencial de produir etanol a partir de recursos sostenibles com ara els residus agrícoles.

En conjunt, aquest treball contribueix tant a la comprensió fonamental com al desenvolupament pràctic de catalitzadors d'alt rendiment per a una producció sostenible d'hidrogen.

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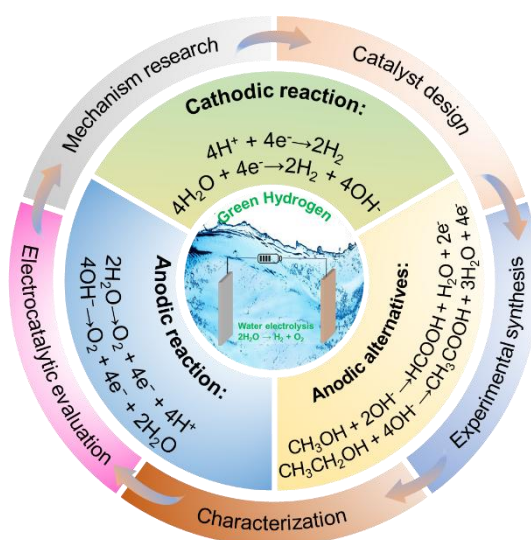
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Chapter 1

Introduction of Current Electrocatalytic Water Electrolysis, Involved Reactions, and Catalyst Design and Optimization Strategies



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Chapter Summary

This chapter addresses the global challenges of decarbonization and fossil fuel substitution, emphasizing water splitting as a key technology and reviewing its most advanced current solutions. As one of the most promising alternatives to fossil fuels, hydrogen energy has encountered significant obstacles in its development as a carbon-neutral carrier, particularly regarding the high cost of water electrolysis associated to the employment of precious elements as electrocatalysts. Therefore, developing electrocatalysts that are both economically viable and exhibit high activity and long-term stability is critical for sustainable hydrogen production. This chapter highlights the need to improve catalyst performance for green hydrogen production, basic theories of related chemical reactions, the state-of-the-art in catalyst design and optimization.

1.1 Energy Crisis and the Rise of Green Energies

With rapid technological advancement and rising per capita consumption, global energy demand has increased significantly.¹ However, energy distribution remains unbalanced and heavily relies on traditional non-renewable fossil fuels.² This dependence has led to recurring energy crises along with severe environmental issues such as greenhouse gas emissions and air pollution associated to the combustion of fossil fuels.^{3–5} The simultaneous rise in atmospheric CO₂ levels, coupled with the ongoing depletion of fossil fuel reserves, underscores the urgent need to transition to renewable energy sources.

Renewable energies offer significant environmental advantages, making them a cornerstone towards zero-CO₂ energy strategies. According to the International Energy Agency (IEA), the capacity of renewable energies is expected to expand significantly in the coming decades, with solar and wind power leading the transition.⁶ Furthermore, accelerating the shift to renewable energies is crucial in the global pursuit of carbon neutrality, particularly in light of international agreements such as the Paris Agreement.⁷

However, the intermittency and supply fluctuations of renewable energies pose challenges to their reliability.⁸ To overcome these issues, advancements in energy storage technologies, including lithium-ion and solid-state batteries, have improved grid stability. In addition, hybrid renewable energy systems, which integrate multiple green energy sources, including solar, wind, hydropower, et, al. can further enhance grid stability, efficiency, and resilience.⁹ By combining these different energy sources, hybrid systems are better able to handle fluctuations and ensure a continuous energy supply.¹⁰ Moreover, global efforts have driven significant cost reductions in solar panels and wind turbines,¹¹ enabling wider deployment. Other renewable sources like biomass, geothermal, and tidal energy contribute to the energy mix, although their deployment depends on specific regional factors.¹²

A fundamental subset of renewable energies, so-called green energies, can significantly reduce environmental impact, lower greenhouse gas emissions, and help mitigate climate change. These refer to energies produced from naturally replenishing sources such as solar, wind or hydro. Despite the promising prospects for green energy, its expansion faces challenges. Among the various forms of green energy, hydrogen has emerged as a highly representative and promising solution, particularly due to its potential to address the intermittency of renewable power sources. For example, during the periods of excess electricity generation, hydrogen can be produced via water electrolysis, effectively stored surplus renewable energy. Conversely, during times of low generation, the stored hydrogen can be used as an energy source through combustion or in fuel cells to supply power back to the grid.

However, hydrogen can be produced through various methods, most commonly fossil fuel reforming and water electrolysis, which will be discussed in the **Section 1.2**. Depending on the energy source and process involved, hydrogen is typically classified into several types: black, grey, blue, yellow, green hydrogen, et al.¹³ Among these, green hydrogen, producing via water electrolysis powered exclusively by renewable energy, enables a zero CO₂ emission and is widely regarded as a key pathway for decarbonization. As such, governments worldwide are actively promoting green hydrogen initiatives. For instance, the European Union (EU) has set ambitious targets as part of its hydrogen strategy, aiming for widespread adoption by 2030.¹⁴ Similarly, countries like Japan and South Korea have outlined hydrogen roadmaps, including large-scale hydrogen infrastructure projects and fuel cell technology development.¹⁵

While green hydrogen holds great promise as a clean energy carrier, its widespread adoption depends on the methods of hydrogen production. The following section introduces the primary hydrogen production technologies, highlighting their advantages, limitations, and ongoing research efforts to enable a sustainable hydrogen economy.

1.2 Hydrogen Production

As a typical representative of green energy, hydrogen possesses a higher energy density ($140 \text{ MJ}\cdot\text{kg}^{-1}$), however, it does not occur naturally on its gaseous or molecular form, but rather as part of other compounds. Hence, hydrogen must be produced through complex chemical processes, including steam methane reforming (SMR), coal gasification, and water electrolysis. Currently, approximately 96% of hydrogen is produced from natural gas and coal, which significantly generating CO_2 emission, contradicting the sustainability principles.¹⁶ In contrast, only 4% of hydrogen production is produced via water electrolysis powered by renewable energy sources has shown great promise as a zero- CO_2 emission cycle.^{16–18} Differing to complex fossil fuel reforming, water electrolysis involves in a simple process, directly delivering hydrogen at the cathode and oxygen at the anode, eliminating carbon emissions as shown in

Figure 1.1.¹⁹

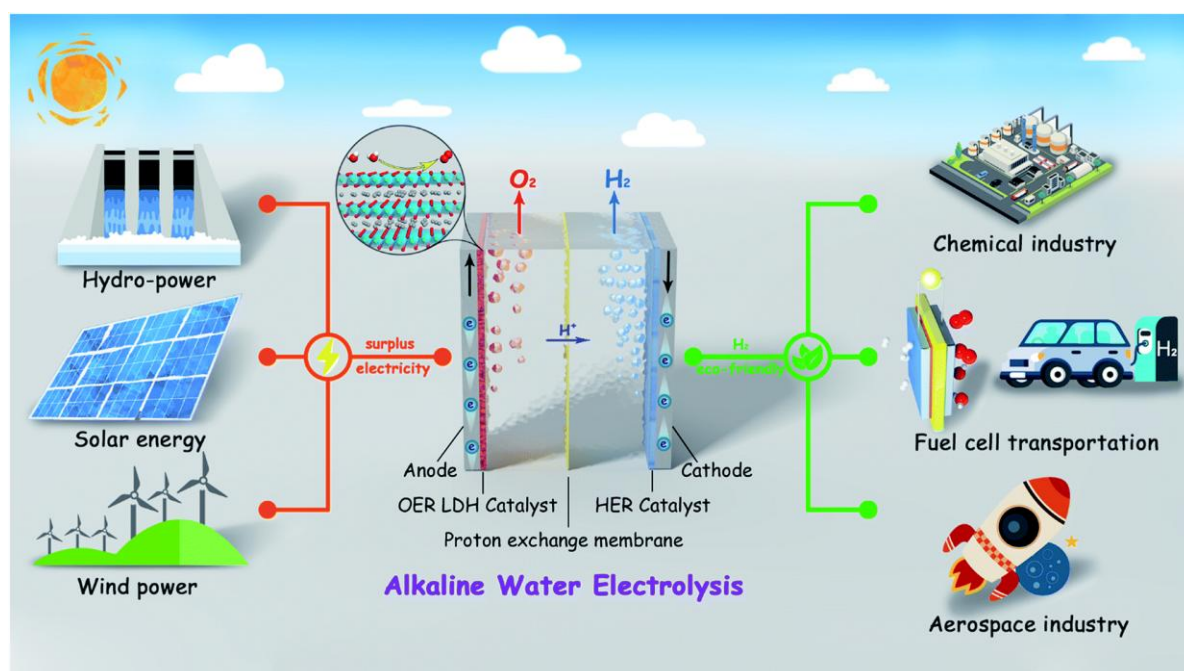


Figure 1.1 Sustainable energy system with integrated water electrolysis for renewable hydrogen production.¹⁹

However, challenges such as high energy input requirements and the cost of

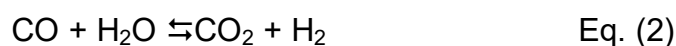
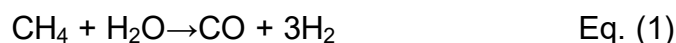
electrolyzers remain significant barrier to widespread application. Current research mainly focuses on developing highly efficient and durable electrocatalysts to reduce electrolyzer costs, and integrating hydrogen storage and transportation systems to enable a viable hydrogen economy.¹⁴

On these grounds, the advancement of green hydrogen is crucial to achieve global sustainable development goals. By fostering continuous technological innovation, implementing supportive policies, and improving hydrogen storage solutions, green hydrogen is expected to play an even more significant role in shaping the future energy landscape. As nations collectively work toward combating climate change and addressing environmental challenges, integrating green hydrogen solutions will be instrumental in transitioning toward a more sustainable and resilient energy system.

1.2.1 Conventional Production: Fossil Fuel Reforming

Currently, large-scale hydrogen production primarily relies on carbon-intensive methods, including SMR, coal gasification, and methanol reforming. These technologies offer high efficiency and scalability but result in significant CO₂ emissions at the same time, leading to serious environmental concerns. A brief introduction about this traditional pathway is below:

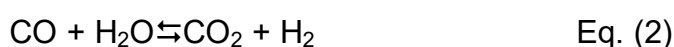
Steam Methane Reforming (SMR): Currently, SMR is the most widely used method for hydrogen production worldwide. In this process, natural gas reacts with steam under high temperature and pressure to produce hydrogen and CO. Subsequently, CO reacts further with water to produce CO₂ and additional H₂. Although SMR offers high efficiency and scalability, it generates significant CO₂ emissions, posing environmental concerns.²⁰ The primary reactions are as follows:



Coal Gasification: Coal gasification involves reacting coal with oxygen and steam at high temperature to produce synthesis gas (syngas, CO and H₂). The CO is then converted into CO₂ and additional H₂ through the water-gas shift reaction similar to SMR.²¹ This method is suitable for coal-rich regions but results in even higher carbon emissions than SMR. The reactions are as follows:



Methanol Reforming: Compared with fossil fuels discussed above, methanol, as a secondary petrochemical product, is also widely used as a hydrogen source. Methanol reforming has distinct advantages over the previously mentioned processes, including lower energy consumption and easier hydrogen separation.^{22,23} The primary reactions are:



While fossil fuel reforming technologies remain dominant, their environmental impact has increasingly spurred interest in cleaner alternatives.

1.2.2 Innovative Pathway: Water Electrolysis

Electrolysis of water is a process that uses electricity to split water into hydrogen and oxygen. This process occurs in an electrolytic cell, where water molecules are broken down into hydrogen and oxygen under the influence of an electric field ([Figure 1.2](#)).²¹ The reactions occurring at the electrodes depend on the acidity or alkalinity of the electrolyte.

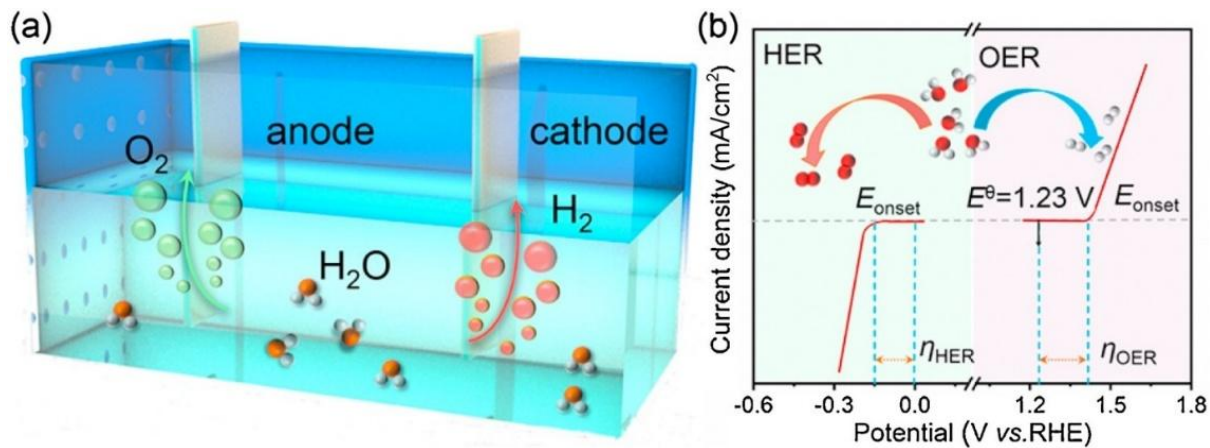
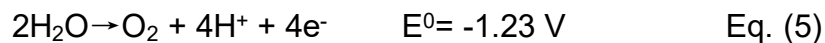
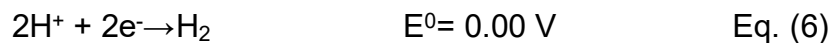


Figure 1.2 (a) The hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) involved in electrocatalytic water splitting. (b) Schematic illustration of the overpotentials associated with HER and OER.²⁴

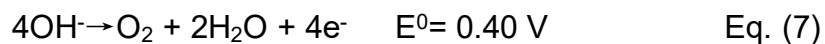
Under acidic conditions, at the anode, the oxidation reaction, known as the oxygen evolution reaction (OER), occurs as:



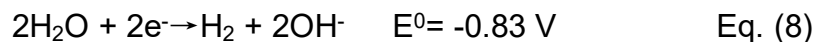
At the cathode, the hydrogen evolution reaction (HER) takes place:



Under alkaline conditions, at the anode, the OER happens as follows:



At the cathode, the HER occurs:



Overall, water electrolysis can be summarized as:



As shown in the reaction equations (Eq. 5-9), the anodic reaction involves a four-electron transfer OER, while the cathode requires a two-electron HER. Under standard conditions, the thermodynamic potential for water electrolysis is 1.23 V versus the reversible hydrogen electrode (vs. RHE). However, due to the sluggish kinetics of both reactions, additional overpotential is typically required to overcome the activation

barrier and system losses, resulting in lower energy conversion efficiency. The actual applied voltage (E_p) for water electrolysis is given by:

$$E_p = 1.23 + \eta_a + \eta_b + \eta_0 \quad \text{Eq. (10)}$$

Where η_a , η_b , and η_0 are the overpotentials associated with the anode, cathode, and other system resistances (e.g., contact and solution resistance), respectively.

The efficiency of this process is influenced by several factors, including the type and concentration of the electrolyte, temperature, current density, the design of the electrolytic cell, et al. Typically, an electrolyte (such as sulfuric acid or potassium hydroxide) is added to the water to increase its conductivity, thereby accelerating the electrolysis reaction. Of course, in order to achieve better efficiency, each parameter needs to be optimized.

In the **next sections (1.3 and 1.4)**, the mechanisms of HER, OER and substituted alcohol oxidation reactions (AOR) and corresponding state-of-the-art will be introduced in detail.

1.3 Water Electrolysis Reactions and Potential Alternatives

As summarized above, water electrolysis stands out as a promising method for carbon-free hydrogen production, utilizing electrochemical reactions at the anode and cathode to split water into oxygen and hydrogen, respectively. The reaction pathways differ under acidic and alkaline conditions, with the OER occurring at the anode and the HER at the cathode as briefly presented in **Section 1.2.2**.

In the following sections, we examine the fundamental electrochemical reactions involved in water splitting and introduce potential alternative anodic reactions aimed at improving energy efficiency and system sustainability.

1.3.1 Cathodic Hydrogen Evolution Reaction (HER)

Following the overview of water electrolysis reactions, the HER serves as the cathodic half-reaction in water electrolysis and has been extensively studied due to its fundamental role in hydrogen production. Particularly, mechanistic insights have been derived from investigations on Pt-based catalysts, which are considered benchmarks for HER activity.¹⁴

It is well established that HER typically proceeds through two consecutive electrochemical steps: The first step, known as the Volmer reaction, involves in the adsorption of protons from the electrolyte onto the catalyst surface coupled with electron transfer, generating adsorbed hydrogen atoms (H_{ads}) as reaction intermediates ([Figure 1.3](#)). The second step refers to the combination of H_{ads} species which can follow two possible pathways to form hydrogen molecular: 1) The Tafel reaction, where two H_{ads} atoms recombine on the surface to release H_2 gas; or 2) The Heyrovsky reaction, where an H_{ads} atom reacts with a proton from the electrolyte and an electron from the electrode to form H_2 .

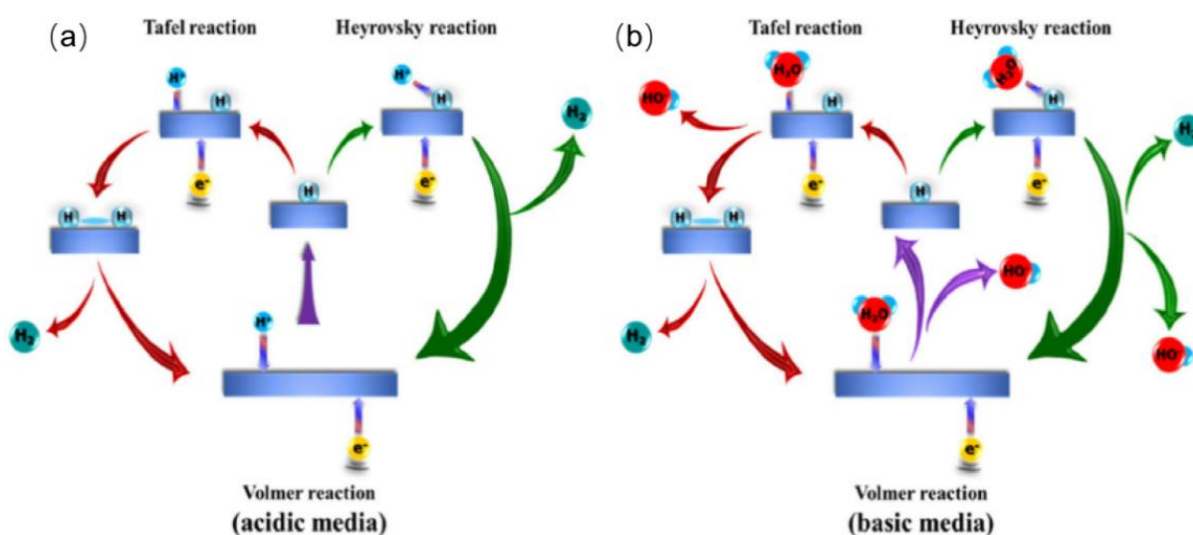


Figure 1.3 The HER pathway in (a) acidic and (b) alkaline media, respectively.²⁵

The above reactions show differences depending on the environment. In acidic media, protons exist primarily as hydrated hydronium ions (H_3O^+), which readily participate in the Volmer reaction. In contrast, in alkaline or neutral media, water molecules act as the proton donor, which introduces additional kinetic barriers and affects the reaction mechanism and rate ([Figure 1.3b](#)). Each of these steps can be characterized by a specific Tafel slope, which provides insight into the rate-determining step (RDS) and overall mechanism ([Table 1.1](#)). The content about Tafel slope will be introduced below.

Table 1.1 Mechanistic pathways of HER electrocatalysis in acid and alkaline medias.²⁶

Steps	Acidic media	Alkaline media	Tafel slope (25°C)
Volmer reaction	$\text{H}^+ + \text{M} + \text{e}^- \rightarrow \text{M-H}_{\text{ads}}$	$\text{H}_2\text{O} + \text{M} + \text{e}^- \rightarrow \text{M-H}_{\text{ads}} + \text{OH}^-$	$\sim 120 \text{ mV} \cdot \text{dec}^{-1}$
Heyrovsky reaction	$\text{M-H}_{\text{ads}} + \text{H}^+ + \text{e}^- \rightarrow \text{M} + \text{H}_2$	$\text{M-H}_{\text{ads}} + \text{H}_2\text{O} + \text{e}^- \rightarrow \text{M} + \text{OH}^- + \text{H}_2$	$\sim 40 \text{ mV} \cdot \text{dec}^{-1}$
Tafel reaction	$2\text{M-H}_{\text{ads}} \rightarrow 2\text{M} + \text{H}_2$	$2\text{M-H}_{\text{ads}} \rightarrow 2\text{M} + \text{H}_2$	$\sim 30 \text{ mV} \cdot \text{dec}^{-1}$
Overall	$4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2$	$4\text{H}_2\text{O} + 4\text{e}^- \rightarrow 2\text{H}_2 + 4\text{OH}^-$	

The catalytic activity of HER is strongly correlated with the Gibbs free energy of H_{ads} (ΔG_{Hads}). According to the Sabatier principle, an optimal catalyst should bind neither strongly nor weakly with the reaction intermediate, facilitating both adsorption and desorption steps efficiently. This relationship is often visualized in volcano plot ([Figure 1.4](#)), where the exchange current density is plotted against the DFT-calculated ΔG_{Hads} .²⁷

The relationship in acidic media is observed in [Figure 1.4a](#), which gives a rise to a characteristic volcano plot that clearly defines two distinct regions. On the one hand, catalysts binding hydrogen too weakly (left hand side of the volcano plot) show insufficient proton adsorption (Volmer step). Conversely, catalysts binding hydrogen

too strongly (right hand side of the volcano plot) suffer from slow hydrogen desorption, which impedes the Heyrovsky or Tafel steps leading to hydrogen poisoning such as the case of gold-based catalysts. Noteworthy, Pt catalysts typically reside at the apex of the volcano, indicating nearly ideal binding strength and hence excellent HER performance.

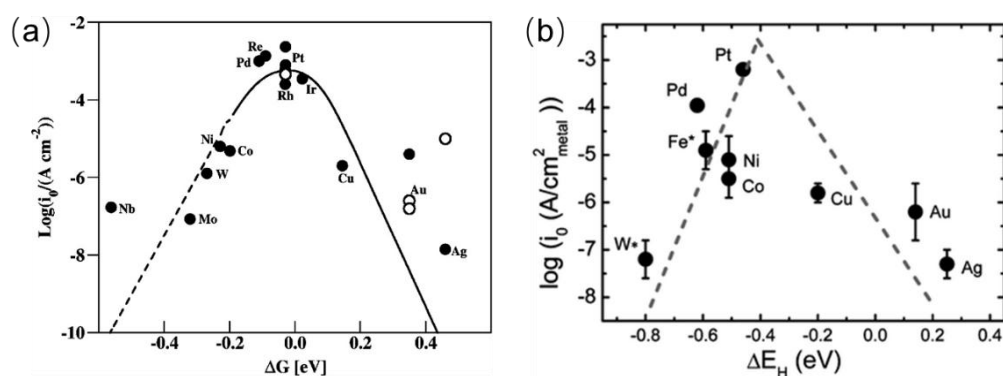


Figure 1.4 Relationship between the i_0 and ΔG_{H^+} in HER volcano plots for various metals in (a) acidic²⁷ and (b) alkaline media.²⁸

Differ to acidic media, alkaline media introduces more complex process. For instance, the involvement of water molecules as proton sources adds an extra energetic barrier, often reducing the overall reaction rate compared to acidic conditions.²⁹ Studies have summarized volcano plots for alkaline HER activity on various metals, with Pt again showing the most favorable position, confirming its status as an almost ideal catalyst for HER in different environments ([Figure 1.4b](#)).

1.3.2 Anodic Oxygen Evolution Reaction (OER)

As the anodic counterpart half-reaction to the HER in water electrolysis, OER plays a crucial role in the overall water electrolysis by providing protons and balancing the charge transfer. Beyond water electrolysis, OER is also a crucial half-reaction in several other energy-related electrochemical systems, including rechargeable metal-air batteries, carbon dioxide reduction (CO_2RR), or nitrogen reduction (N_2RR) reactions,

making it indispensable in electrochemical energy conversion technologies.³⁰ As discussed above, water splitting involves the coupling of OER and HER, and under standard conditions, the thermodynamic oxidation potential is 1.23 V vs. RHE (Eq. 9). Unlike HER, OER involves a four-electron transfer process with multiple intermediate steps ([Table 1.2](#)). The complexity leads to inherently sluggish reaction kinetics, requiring high overpotentials to proceed at practical rates, which represents a major bottleneck limiting the overall efficiency of water electrolysis.

Table 1.2 Mechanistic pathways of OER electrocatalysis in acid and alkaline medias.³¹

Steps	Acidic media	Alkaline media
1	$2\text{H}_2\text{O} + \text{M} \rightarrow \text{M-OH} + \text{H}_2\text{O} + \text{e}^- + \text{H}^+$	$\text{OH}^- + \text{M} \rightarrow \text{M-OH} + \text{e}^-$
2	$\text{M-OH} + \text{H}_2\text{O} \rightarrow \text{M-O} + \text{H}_2\text{O} + \text{e}^- + \text{H}^+$	$\text{M-OH} + \text{OH}^- \rightarrow \text{M-O} + \text{H}_2\text{O} + \text{e}^-$
3	$\text{M-O} + \text{H}_2\text{O} \rightarrow \text{M-OOH} + \text{e}^- + \text{H}^+$	$\text{M-O} + \text{OH}^- \rightarrow \text{M-OOH} + \text{e}^-$
4	$\text{M-OOH} \rightarrow \text{M} + \text{O}_2 + \text{e}^- + \text{H}^+$	$\text{M-OOH} + \text{OH}^- \rightarrow \text{M} + \text{O}_2 + \text{H}_2\text{O} + \text{e}^-$
Overall	$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{e}^- + 4\text{H}^+$	$4\text{OH}^- \rightarrow \text{O}_2 + 4\text{e}^- + 2\text{H}_2\text{O}$

Similar to HER, in [Figure 1.5](#), the catalytic activity of OER can also be characterized by a volcano plot, which represents the relationship between the binding energies of specific intermediates and the overall catalytic performance.^{32,33} It can be observed that materials based on the oxides of Ir and Ru exhibit relatively high catalytic activity, either in acidic or alkaline medias, positioning them near the top of the volcano plot. These noble metal oxides possess optimal adsorption energies for key OER intermediates, enabling efficient reaction kinetics. As a result, they are widely regarded as benchmark catalysts for OER, despite their scarcity and high cost.

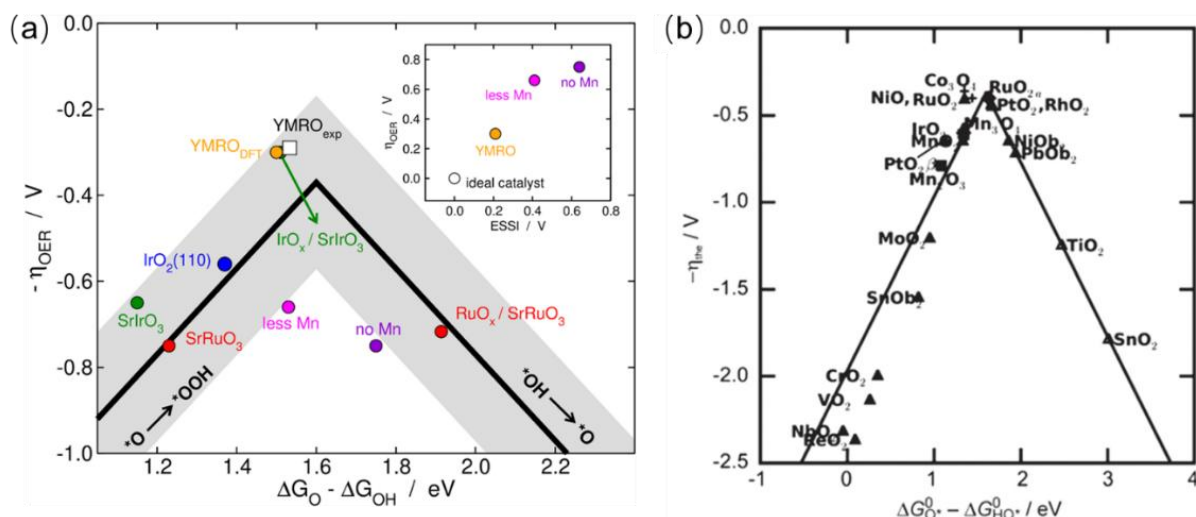


Figure 1.5 Relationship between the η_{OER} and $\Delta G_{O^*} - \Delta G_{OH^*}$ in OER for various metals in (a) acidic³³ and (b) alkaline media.³²

Currently, two main catalytic mechanisms for OER are widely recognized^{34–36}: the adsorbate evolution mechanism (AEM) and the lattice oxygen mechanism (LOM). As shown in [Figure 1.6](#), both mechanisms share the initial two elementary steps, although in some cases, specific situations may require case-by-case analysis. After these common steps, the mechanisms diverge, proceeding through different intermediates and exhibiting distinct catalytic behaviors. The detailed reaction pathway and mechanistic differences between AEM and LOM will be discussed below.

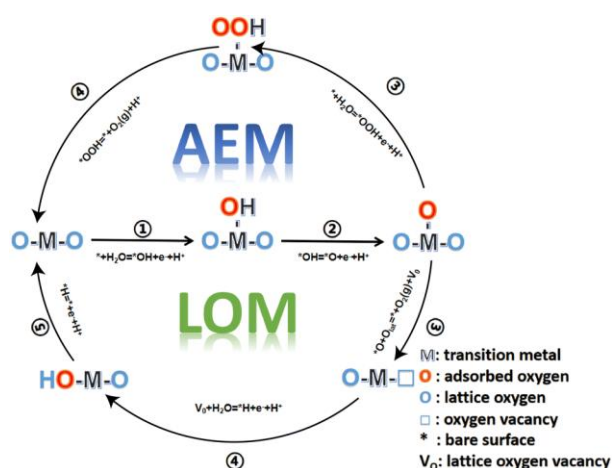


Figure 1.6 Comparison of the adsorbate evolving mechanism (AEM) and lattice oxygen mechanism (LOM).³⁴

Adsorbate Evolution Mechanism (AEM):

The AEM is one of the most commonly studied reaction pathways for the OER, especially on transition metal-based catalysts. In this mechanism, the reaction typically occurs at a single metal atom site (denoted as M) on the catalyst surface, involving four proton and electron transfers, ultimately leading to the generation of oxygen molecules from water.

As shown in [Figure 1.7a](#), the reaction proceeds through formation of three key intermediates: $^*\text{OH}$, $^*\text{O}$, and $^*\text{OOH}$ via the following steps:

1. OH^- adsorption: Hydroxide ions (OH^-) from the electrolyte adsorb onto M sites on the catalyst surface, forming M-OH intermediate.
2. Deprotonation: The M-OH species undergo deprotonation reaction, yielding the formation of M-O intermediate.
3. O-O bond formation: The M-O intermediate reacts with another OH^- to form the M-OOH intermediates, an essential precursor to oxygen generation.
4. Deprotonation and oxygen release: Finally, M-OOH undergoes deprotonation, releasing O_2 gas and regenerating the M sites for next catalytic cycle.

The thermodynamics of these steps are reflected in the free energy changes (ΔG), illustrated in [Figure 1.7a](#). Ideally, for a catalyst to operate with zero overpotential, the free energy change for each step should be 1.23 eV (at $U = 0$ V vs. RHE), which corresponds to the standard thermodynamic potential for OER. However, in practice, such ideal performance is not observed due to inherent imitations governed by linear scaling relationships between the adsorption energies of $^*\text{OH}$, $^*\text{O}$, and $^*\text{OOH}$.

Specifically, $^*\text{OH}$ and $^*\text{OOH}$ tend to bind to the surface via a single oxygen atom, resulting in similar adsorption geometries and thus strongly correlated energies. As shown in [Figure 1.7b](#), the energy difference between $\Delta G_{^*\text{OOH}}$ and $\Delta G_{^*\text{OH}}$ is consistently

around $\sim 3.2 \pm 0.2$ eV, regardless of catalyst material or binding site.³⁷

This intrinsic correlation has several important implications:

1. Reduced computational cost: Since ΔG^*_{OOH} is linearly related to ΔG^*_{OH} , the former can be estimated from the latter, reducing the computational cost of evaluating and predicting catalytic activity.
2. Minimum theoretical overpotential: The minimum energy required for two sequential steps (ideally 2×1.23 eV = 2.46 eV) is lower than the actual value (~ 3.2 eV). This leads to a theoretical lower bound overpotential of approximately 0.37 eV ($(3.2 - 2.46)/2$ eV), which has been validated experimentally.³⁷
3. Universal activity descriptor: Since ΔG_1 and ΔG_4 (Figure 1.7a) are rarely the RDS, the difference $\Delta G^*_{\text{O}} - \Delta G^*_{\text{OH}}$ can serve as a universal activity descriptor for predicting the OER performance of various materials.

Accordingly, the OER overpotential under the AEM framework can be estimated by the following equation:

$$\eta_{\text{OER}} = \{\max[(\Delta G^*_{\text{O}} - \Delta G^*_{\text{OH}}), 3.2 \text{ eV} - (\Delta G^*_{\text{O}} - \Delta G^*_{\text{OH}})]/e\} - 1.23 \text{ V} \quad \text{Eq. (11)}$$

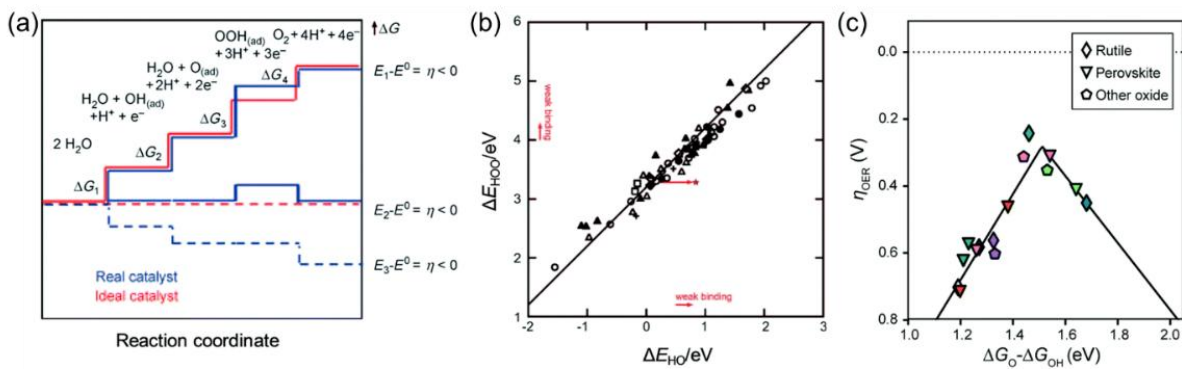


Figure 1.7 (a) Gibbs free energies at $U = 0$ for ideal and actual catalysts. (b) Correlation between the adsorption energies of *OOH and *OH on various oxides, including perovskite, rutile, anatase, Mn_xO_y , Co_3O_4 , and NiO .³⁸ (c) OER volcano plot for rutile, perovskite, and other oxide catalysts.³⁷

In summary, while AEM provides valuable mechanistic insights into OER, it is

inherently constrained by thermodynamic scaling laws between key intermediates. These limitations result in a fundamental lower bound on the overpotential (~ 370 mV) that even the best-performing catalysts cannot avoid.³⁹ Consequently, future advancements in OER catalyst design must therefore focus on identifying strategies or materials capable of circumventing these scaling relationships to break through current performance limits.

Lattice Oxygen Mechanism (LOM):

In contrast to the AEM, the LOM process involves the direct participation of lattice oxygen atoms within the catalyst structure, which distinguishes it from AEM. According to LOM theory, the mechanism can be described as follows:

1. Lattice oxygen activation: Oxygen atoms within the crystal lattice of the catalyst become activated under electrochemical conditions, enabling their direct participation in the reaction.
2. O-O bond formation: Two activated lattice oxygen atoms, or one activated lattice oxygen and one oxygen atom from electrolyte, couple to form an O-O bond, generating O_2 directly without the formation of $*OOH$ intermediates, as required in AEM.
3. Oxygen vacancy creation: The release of lattice oxygen during the reaction creates oxygen vacancies (O_v) within the catalyst structure. These vacancies are essential for sustaining the reaction cycle.
4. Vacancy replenishment by OH^- : OH^- from the electrolyte replenish the O_v , restoring the catalyst's lattice integrity and enabling continuous catalytic turnover.

One important difference between LOM and AEM lies in the RDS. In LOM, the RDS is not hindered by the energy difference ($\Delta G^*_{OOH} - \Delta G^*_{OH}$) as observed in AEM. As a result, the theoretical minimum overpotential achievable via LOM is not constrained by the approximate 370 mV limitation inherent to AEM catalysts, offering potential for more

efficient OER performance.

With ongoing theoretical and experimental developments, the LOM reaction pathway has been further refined, including oxygen vacancy site mechanisms (OVSM), single-metal site mechanisms (SMSM), and dual-metal site mechanisms (DMSM), as illustrated in [Figure 1.8](#).⁴⁰ OVSM emphasizes the role of dynamically formed O_v as active sites; SMSM focuses on localized lattice oxygen activation at individual metal centers; while DMSM highlights cooperative interactions between adjacent metal atoms to facilitate O-O bond formation. As more advanced experimental and theoretical characterization, the theories of mechanism are continuously developing.

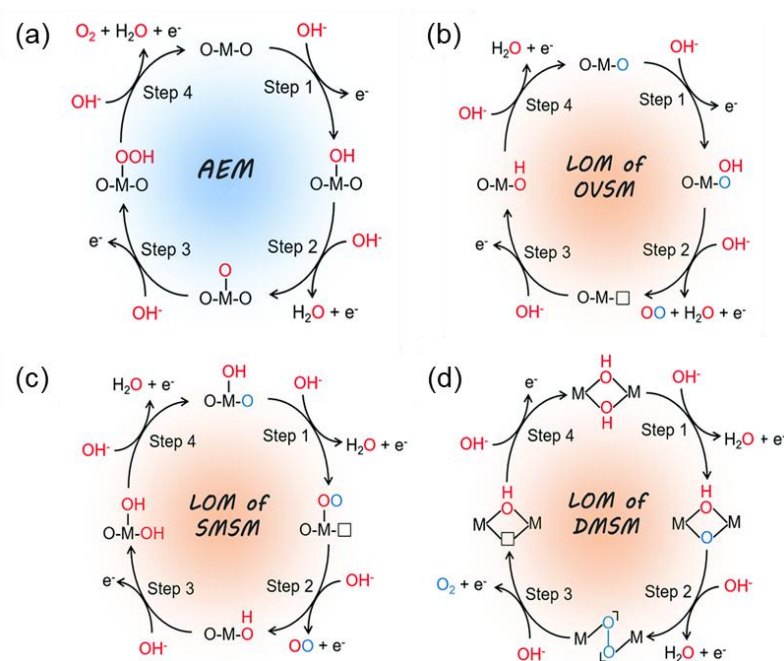


Figure 1.8 Different reaction pathways for OER. (a) Schematic illustration of the AEM pathway in alkaline media on an active metal site. The lattice oxygen and oxygen from the electrolyte are marked in black and red colors, respectively. (b-d) Schematic illustrations of three alternative pathways of LOM in alkaline media, each involving a different catalytic center: (b) Oxygen-vacancy-site mechanism (OVSM), (c) single-metal-site mechanism (SMSM), and (d) dual-metal-site mechanism (DMSM). In panels (b-d), chemically inert lattice oxygen, active lattice oxygen involving in OER, and oxygen from the electrolyte are marked in black, blue, and red colors, respectively, and $\square$ represents lattice O_v .

Despite their differences, all LOM-related pathways share the fundamental principle of lattice oxygen involvement in OER. A comprehensive understanding of these mechanisms requires system-specific analysis, integrating both theoretical modeling and experimental validation tailored to the specific catalyst system. These distinctions highlight the importance of matching mechanistic understanding with material design strategies in the development of high-performance OER catalysts.

In order to characterize the real participation of lattice oxygen in the reaction, several methods have been developed based on its unique mechanistic properties. First, due to the intrinsic reliance on lattice oxygen participation and redox flexibility, the LOM exhibits pH dependence.^{41,42} In alkaline media, abundant OH⁻ facilitates deprotonation and stabilizes O_v, promoting O-O bond formation via lattice oxygen. In contrast, acidic conditions hinder these processes and often destabilize the catalyst structure, limiting the development of efficient acidic OER catalysts. This pH sensitivity is further pronounced in nonconcerted proton-electron transfer steps, where decoupled proton transfer is highly dependent on local proton activity, and thus to the electrolyte pH.

Second, the formation of peroxide species (O₂²⁻/O⁻) intermediates, which is special happening in LOM rather than AEM, can be probed using tetramethylammonium cation (TMA⁺) as a chemical marker.^{40,43} TMA⁺ owns the property to block the further reaction of O₂²⁻ species, thereby serving as an effective indicator of the LOM pathway.

Third, isotope-labeled experiments using H₂¹⁸O as electrolyte coupling with real-time differential electrochemical mass spectrometry (DEMS) is a direct method to identify LOM.^{44,45} The signals of ¹⁸O¹⁶O or ¹⁶O¹⁶O confirm the involvements of lattice oxygen in the oxygen evolution process.

In addition to these methods, advanced spectroscopic techniques such as X-ray absorption spectroscopy (XAS) and theoretical approaches like density functional theory (DFT) simulations are also widely employed to gain mechanistic insights into LOM.⁴⁶

1.3.3 Alcohol Oxidation Reaction (AOR)

As mentioned above, the water electrolysis process is significantly hindered by the high overpotential to initiate the OER and sluggish kinetics. These issues not only limit reaction efficiency but also represent a major barrier to the large-scale commercialization of water electrolysis technologies. Moreover, although O_2 is produced at the anode, its industrial value is relatively low compared to hydrogen, undermining the overall economic feasibility of the process. While O_2 has established applications in areas such as chemical production and medical uses, it is more efficient and cost-effectively produced through air separation techniques, making it more reasonable to replace OER by other favorable reactions.

Since it is frequently the RDS due to its multistep, four-electron transfer mechanism, making it require higher energy input, thereby reducing overall system efficiency. Moreover, safety concerns arise from the potential mixing of H_2 and O_2 gases, which can lead to the formation of explosive H_2/O_2 mixture under certain conditions.^{47,48}

In light of these issues, an alternative strategy known as hybrid electrocatalytic water splitting has been proposed. In this approach, the sluggish anodic OER is replaced by more thermodynamically favorable organic oxidation reactions, coupling with cathodic HER ([Figure 1.9](#)).⁴⁹ This method can significantly lower the overall cell voltage, enhance energy efficiency, reduce explosion risk, and simultaneously generate value-added chemical products at the anode in some cases.^{50–52} As a result, this dual benefit improves both the technical and economic viability of hydrogen production systems.

Several important criteria should be considered when selecting the suitable alternatives.⁵³ First, the reactants should be water-soluble under ambient conditions to ensure practical operation. Second, their oxidation potential must be lower than that of OER, enabling a more energetically favorable process. Third, the reactants and products of the anodic reaction should not interfere with or degrade the cathodic HER performance. Finally, it is highly desirable that the products from the anodic reactions

have relevant interest for industrial applications, thereby enhancing the economic efficiency of the entire system.

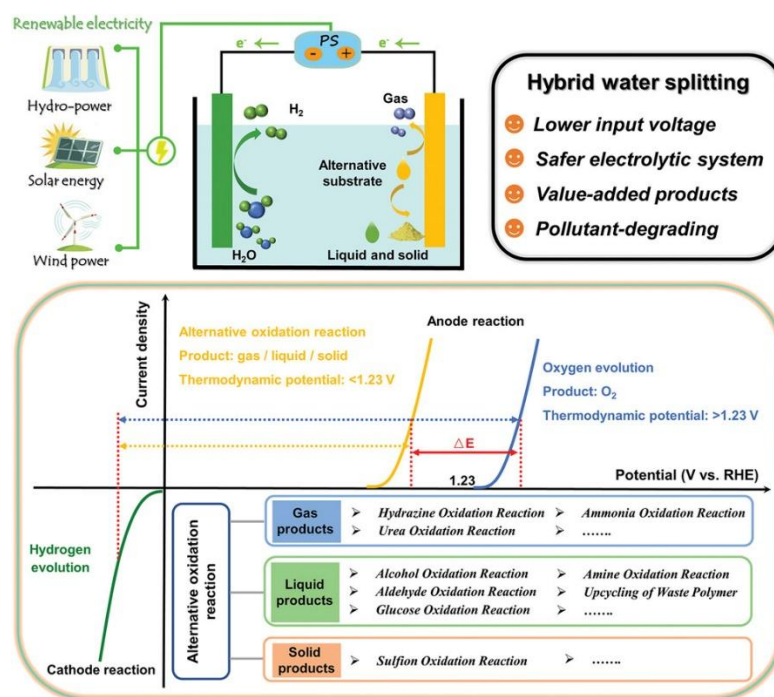


Figure 1.9 Illustrates the hybrid water splitting system by replacing the OER with alternative anodic oxidation reactions.⁴⁹

In recent years, various compounds including urea,⁵⁴ hydrazine,⁵⁵ and alcohols,^{56,57} have been developed as potential alternatives for hybrid water electrolysis. Among these, alcohol electrooxidation coupled with HER has attracted particular attention, owing to the favorable properties of alcohols as substrates.^{58,59}

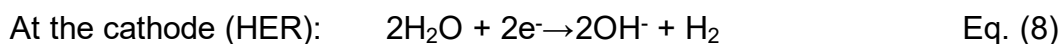
Alcohols constitute a class of organic compounds characterized by the presence of at least one hydroxyl (-OH) group attached to a carbon atoms or side chains on aromatic rings. Common alcohols include methanol, ethanol, ethylene glycol, glycerol, benzyl alcohol, et al. Notably, methanol and ethanol have attracted widespread research interest due to their low cost, high activity, and abundant resources,^{60,61} making them ideal candidates for sustainable hydrogen production.

Methanol Oxidation Reaction (MOR)

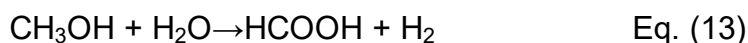
Methanol is a colorless liquid with a density of $0.79 \text{ g}\cdot\text{cm}^{-3}$ at 20°C and a boiling point of 65.15°C under atmospheric pressure. Notably, it has a high hydrogen content of $12.6 \text{ wt}\%$,⁶² which makes it a promising candidate for hydrogen-related applications. Its relatively simple molecular structure, with only one carbon atom, facilitates more controllable oxidation pathways and reduces the formation of undesirable byproducts. The theoretical thermodynamic oxidation potential for methanol is approximately 0.10 V , considerably lower than that for the OER, indicating that methanol oxidation is energetically favorable and can potentially reduce the energy consumption of electrolysis.^{63,64}

Industrial methanol production predominantly involves chemical synthesis by precisely controlling the ratio of CO and H_2 under temperature and pressure conditions. Nevertheless, methanol is a neurotoxic compound with significant anesthetic effects and has been reported to cause brain edema, with particularly toxicity to the optic nerve and retina.³⁷ Additionally, the oxidation products, formaldehyde, and formic acid are more toxic than methanol itself and can lead to metabolic disorders and severe ocular damage if not properly managed.

When methanol oxidation reaction is coupled with hydrogen evolution in alkaline conditions, the reaction proceeds as follows:



The overall reaction can be summarized as:



Additionally, HCOOH can be further oxidized into CO or CO_2 to complete the reaction. However, this results in additional carbon emissions, which contradict the principle of green and sustainable chemistry. In contrast, the selective conversion of methanol to

value-added HCOOH is more economical and environmentally favorable. Moreover, this process enables hydrogen production at a lower cell voltage compared to conventional water electrolysis, thus improving overall energy efficiency.

Ethanol Oxidation Reaction (EOR)

Ethanol, like methanol, is a colorless liquid with a density of 0.79 g·cm⁻³ at 20 °C and a boiling point of 78.3 °C under atmospheric pressure. It has a hydrogen content of 13.0 wt%, slightly higher than methanol. Similar to methanol, ethanol can be produced via ethylene hydration reaction,³⁷ but more interesting, it can be produced through biomass fermentation mainly through microbial fermentation of sugars or enzymatic hydrolysis of starch-rich materials, the so-called bioethanol.⁶⁵ This bio-based production method has remained stable and widely applied for decades and offers potential for a sustainable fuel production cycle.

In 2010, Pei Kang Shen and colleagues experimentally demonstrated that ethanol oxidation in alkaline media requires a thermodynamic potential substantially lower than that of the OER in conventional water electrolysis.⁶¹ This finding underscores ethanol's suitability as an anodic reactant to reduce energy input. The specific reactions are as follows⁶⁶:

Cathodic HER:



Anodic ethanol oxidation:



Overall balanced reaction:



This reaction system not only reduces the voltage required for electrolysis but also generates acetic acid or acetate salts, which are commercially valuable chemicals. Thus, coupling ethanol oxidation with HER can improve the overall economic and

energy efficiency of hydrogen production compared to traditional water splitting.

However, like MOR, ethanol oxidation faces challenges, such as the formation of byproducts like acetaldehyde and formic acid, which lower the reaction's selectivity. Additionally, the slower kinetics due to the presence of C-C bonds in ethanol require higher energy input and more stringent conditions. Over-oxidation into CO or CO₂ is also common, complicating process control. Furthermore, catalysts need to be more resistant to deactivation and more durable, as ethanol oxidation can lead to catalyst surface contamination. These factors make ethanol oxidation more complex and less efficient than MOR, despite its potential economic benefits.

1.4 Electrocatalysts for HER, OER and AOR

As previously discussed, electrocatalysts play a key role in determining the efficiency, energy consumption, and practical viability of electrochemical processes such as water or alcohol-water electrolysis. Their ability to lower the required overpotential directly influences the rate of HER, OER and AOR, thereby impacting the overall performance and cost-effectiveness of the system.

Currently, most commercial electrocatalysts are based on noble metals, including platinum on carbon (Pt/C) for HER and AOR, iridium oxide (IrO₂) and ruthenium oxide (RuO₂) for OER, and palladium on carbon (Pd/C) for AOR. Although these materials exhibit outstanding catalytic activity and are widely used as performance benchmarks, their high cost, scarcity, and in some cases, limited long-term stability, pose major obstacles to their large-scale application in practical energy systems. Additionally, degradation of noble metal catalysts during prolonged electrolysis increases maintenance demands and contributes to overall system inefficiency.

To overcome these limitations and promote the economic and environmental sustainability of electrolysis technologies, two general strategies are being pursued:

on the one hand, developing non-noble metal catalysts with high intrinsic activity, structural robustness, and chemical stability in relevant electrochemical environments. On the other hand, optimizing existing high-performance catalysts through structural engineering, surface modification, elemental doping, and support modification, aimed at reducing metal loading while maintaining or enhancing performance.

Building upon these directions, the present study focuses on integrating rational catalyst design strategies into existing high-activity catalyst systems and improve both electrocatalytic activity and operational durability. In the following sections, we systematically review recent advances and application prospects of representative catalysts for HER, OER, and AOR, respectively.

1.4.1 Electrocatalysts for HER

As previously mentioned, Pt is known as one of the most active catalysts for the HER, exhibiting excellent electrocatalytic performance in both acidic and alkaline media ([Figure 1.4](#)). The commercial Pt/C catalysts, prepared by dispersing Pt nanoparticles on carbon black support, have served as a benchmark material in HER research.²⁷ Therefore, the optimization of Pt-based materials remains an important strategy for improving HER performance.

However, due to the limited tunability of monometallic Pt, researchers have explored several approaches to improve its utilization efficiency and catalytic activity. One widely adopted strategy is the size reduction of Pt particles, which increases the number of exposed active sites. This approach has led to the development of single-atom catalysts (SACs). However, Pt SACs are easy to suffer from aggregation, reducing stability. To overcome this issue, Pt SACs are often anchored onto carbon-based or two-dimensional substrates.^{67,68} For example, Wei Chen's team successfully constructed four Pt SACs on MoS₂, WS₂, MoSe₂, and WSe₂ substrates, respectively, using a site-specific electrodeposition method, achieving mass activities 73 times and

43 times higher than commercial Pt/C in acidic and alkaline media, respectively.⁶⁸

Moreover, combining Pt with other metals to form bimetallic even high-entropy alloys is another important strategy for enhancing catalytic performance. For instance, Yusuke Yamauchi and colleagues synthesized various mesoporous binary Pt-M alloy films (m-Pt-M, M = Pd, Rh, and Ru) with uniform pore sizes and element distribution, among which m-Pt-Ru exhibited a mass activity 17.8 times higher than that of Pt/C.⁶⁹ Similarly, Hui Sun et al. synthesized ultrafine PtCo bimetallic nanoparticles, achieving a low overpotential of 27.3 mV and a high mass activity of $4.73 \text{ A} \cdot \text{mg}^{-1}_{\text{Pt}}$.⁶⁷ With the deepening understanding of high-entropy alloys (HEAs) systems, Yizhong Huang's group employed laser pulse irradiation to fabricate FeCoNiCuPtIr six-element HEA catalysts on carbon nanotube (CNTs) surfaces. These catalysts exhibited ultralow overpotential (21 mV @ $-10 \text{ mA} \cdot \text{cm}^{-2}$), a small Tafel slope ($54.5 \text{ mV} \cdot \text{dec}^{-1}$), and stability over 20 hours of continuous operation.⁷⁰

In addition to Pt-based materials, recent years have witnessed extensive research into the application of transition metal compounds for HER, such as transition metal chalcogenides,⁷¹ nitrides,⁷¹ phosphides,^{72,73} and carbides.⁷⁴ Among these, transition metal dichalcogenides (e.g., MoS_2) have been widely investigated as Pt substitutes due to their unique layered structure, abundant edge sites, good chemical stability, and low cost.⁷⁵ Their main advantage lies in the high catalytic activity at the edge regions, making them well-suited for HER. However, several challenges are waiting to overcome: the basal planes are usually catalytically inert, limiting overall activity; the inherent electrical conductivity is low, hindering efficient electron transport; and their catalytic performance in alkaline or neutral media is generally inferior to that in acidic environments, with stability also requiring improvement. To address these issues, current research focuses on strategies such as doping, defect engineering, and heterostructure design to enhance conductivity, activate basal planes, and improve structural stability.

1.4.2 Electrocatalysts for OER

As previously mentioned, compared to the HER, the OER is considered the primary bottleneck limiting the overall efficiency of water electrolysis due to its intrinsically sluggish kinetics and high energy barrier. This issue is particularly pronounced under acidic conditions, where the variety of available OER catalysts remains extremely limited. Current research in this area mainly focuses on noble-metal-based materials such as IrO_2 and RuO_2 , along with their binary and ternary composite oxides, perovskite oxides, and spinel structures.⁷⁴ Although these materials exhibit excellent catalytic performance and are considered benchmarks for acidic OER, their high cost and scarcity pose significant challenges for large-scale deployment.

In contrast, OER catalyst development under alkaline conditions is more mature. Research has increasingly turned to cost-effective and earth-abundant transition metal compounds such as oxides, hydroxides, nitrides, and phosphides based on metals like Fe, Co, Ni, and Mn.^{76–78} Among these, layered double hydroxides (LDH) have attracted considerable attention due to their high specific surface area, tunable layered structure, unique electronic density of states, abundant electron transfer pathways, and intrinsic catalytic activity and stability. Notably, Markovic and co-workers established a general activity trend among 3d transition metal hydroxides in alkaline media as $\text{Ni} > \text{Co} > \text{Fe} > \text{Mn}$, combining both experimental and theoretical evidence.⁷⁹

As research has advanced, increasing focus has been placed on Ni- and Fe-based LDH materials. For example, Alexis T. Bell's team demonstrated that the introduction of trace Fe impurities into Ni-based hydroxides could significantly enhance their OER activity by promoting the in-situ formation of a NiFe-LDH phase during operation.⁷⁹ This process effectively reconstructs the catalyst structure, activating the catalytic sites.

Despite their strong performance, the underlying catalytic mechanism of NiFe LDH and identification of the active sites remain controversial. For instance, Louie et al. proposed that Ni is the primary active site, existing predominantly as NiOOH during

OER, while Fe doping modifies the electronic structure by lowering the average oxidation state of Ni to enhance activity.⁸⁰ In contrast, Klaus et al. suggested that Fe incorporation directly induces the formation of highly active LDH phases,⁸¹ while Friebe and Lee provided spectroscopic and structural evidence supporting Fe as the active site.⁸² Despite these differing viewpoints, NiFe LDH remains widely regarded as one of the most promising OER catalysts due to its high activity and structural versatility.

To further enhance the performance of LDH based catalysts, researchers have explored various strategies, including oxygen vacancies (O_v) and structural defects, exfoliating nanosheets to increase the exposure of active sites, and doping with various metal elements to modulate the electronic structure. For example, recent studies have reported significant improvements in catalytic activity through the incorporation of high-density O_v and nanoscale hexagonal defects.⁸³ As for the detailed optimization methods for catalysts, we will demonstrate in **Section 1.5.2**.

In addition, LDH materials are often subjected to post-synthetic treatments such as phosphorization, carbonization, or sulfurization to form the corresponding phosphides, carbides, or sulfides. These derived materials typically exhibit enhanced electrical conductivity and structural robustness. However, during OER processes, the active sites on the surface are often reconstructed into metal hydroxide or oxyhydroxide, while the underlying phosphide or other phases primarily serve as conductive supports and structural backbones.^{84,85}

1.4.3 Electrocatalysts for AOR

Compared to the conventional OER, which typically requires a high overpotential and exhibits sluggish kinetics, the AOR has emerged as a promising alternative anodic reaction. Particularly when coupled with the HER in hybrid alcohol-water electrolysis systems, AOR can significantly reduce the overall cell voltage, enhance energy efficiency, and generate value-added organic products, offering both energetic and

economic advantages.

Currently, catalysts for AOR are broadly categorized into noble metal-based catalysts (primarily Pt- and Pd-based) and non-noble metal catalysts. Pt and Pd-based catalysts exhibit excellent electrocatalytic activity toward the oxidation of small alcohols such as methanol and ethanol. These materials are capable of facilitating deep oxidation pathways, converting alcohols into CO or CO₂ and releasing multiple electrons per molecule, thereby contributing to high anodic current densities and efficient charge transfer.⁸⁶

However, several significant drawbacks limit their broader application: on one hand, the complete oxidation pathway yields carbon emissions, which is opposite to the goal of carbon-neutral energy systems. On the other hand, strongly adsorbed intermediates like CO can form during the reaction, causing catalyst poisoning and progressive loss of activity, especially in extended or large-scale electrolysis operations. For instance, Qin et al. synthesized HEA ultrathin nanowires composed of PtRuNiCoFeGaPbW, which exhibited outstanding catalytic performance for methanol oxidation, but still faced the aforementioned challenges.⁸⁷

In contrast, non-noble metal catalysts (such as Ni, Fe, Co, and Cu) have attracted increasing attention in recent years. Although these materials generally require higher voltages to activate and dehydrogenate alcohol molecules, their low cost, abundant availability, and superior product selectivity present great potential for sustainable energy systems. These catalysts often lead to forming liquid products such as formic acid or acetic acid during alcohol oxidation, which possess higher commercial value and thus contributes to improving the overall economy.

Notably, several high-active non-noble metal catalyst systems have been developed in recent years. For example, Kang et al. synthesized a Cu@CoO_x core-cage nanostructure, which exhibited excellent catalytic activity and long-term durability for

MOR.⁸⁸ In this work, the Cu core facilitates the adsorption of methanol molecules, while the outer CoO_x shell, which is partially oxidized to higher valence states, provides efficient electron transfer and reactive sites. The synergistic interaction between these two components contributes to high catalytic efficiency and structural robustness during operation.

In summary, although noble metal catalysts remain the performance benchmark for AOR, their drawbacks, including cost, scarcity, and poisoning issue, have motivated the exploration of non-noble metal systems as sustainable alternatives. With ongoing advancements in material design, nanostructuring, and interface engineering, non-precious metal catalysts are expected to play a key role in hybrid alcohol-water electrolysis systems for simultaneous hydrogen and value-added chemical production.

1.5 Electrocatalysts Preparation and Optimization

As we have outlined, electrocatalysts play a crucial role in electrochemical reactions such as water electrolysis, fuel cells, and CO_2 reduction. Their catalytic activity, stability, and efficiency are primarily governed by factors such as composition, morphology, surface structure, and electronic properties.⁸⁹ These properties are highly influenced by the synthesis methods and design strategies employed during catalyst fabrication.

Among the available synthesis techniques, including gas-phase methods (e.g., chemical vapor deposition) and solid-state reactions offer high crystallinity and purity but often require extreme temperatures, expensive equipment, and present scalability challenges.⁹⁰ In contrast, wet-chemical approaches provide a versatile, scalable, and cost-effective platform for tailoring catalyst properties at the nanoscale, enabling fine control over particle size, composition, crystal phase, and active site distribution, all of which are critical to enhancing electrocatalytic performance.

1.5.1 Typical Synthetic Methods: Wet-Chemical Approaches

Common wet-chemical approaches include microwave (MW)-assisted synthesis, hydrothermal/solvothermal methods, sol-gel synthesis, electrodeposition, and co-precipitation. These methods can also be combined with post-treatments such as gas-phase reduction to obtain metallic phases or with oxidative treatments to increase the oxidation state of the final material. Among them, MW-assisted synthesis and hydrothermal synthesis have emerged as their specific properties. The following sections focus on these two representative techniques and the optimization strategies for electrocatalysts.

Microwave (MW)-assisted Synthesis

MW radiation is an electromagnetic wave with frequencies ranging from 0.3 to 300 GHz, corresponding to wavelengths from 1 mm to 1 m. The heating effect induced by MW radiation primarily arises from dipolar polarization and ionic conduction, as illustrated in [Figure 1.10](#).⁹¹ When a reaction medium is exposed to MW radiation, polar molecules or ions within the material attempt to realign with the rapidly oscillating electric field. This continuous reorientation causes molecular friction and dielectric loss, ultimately resulting in heat generation.⁹² However, when the magnetic field frequency is much higher than the response time of the dipoles, they fail to keep up with the rapid reorientation, resulting in negligible heat generation. Conversely, at the commonly used frequency of 2.45 GHz, many polar molecules in liquids lag behind the oscillating electric field, causing significant resistive heating through dielectric loss. Additionally, ionic conduction contributes substantially to heating, as dissolved charged particles oscillate and collide with neighboring molecules under MW irradiation. Notably, ionic conduction generally has a stronger heating effect compared to dipolar polarization.⁹³

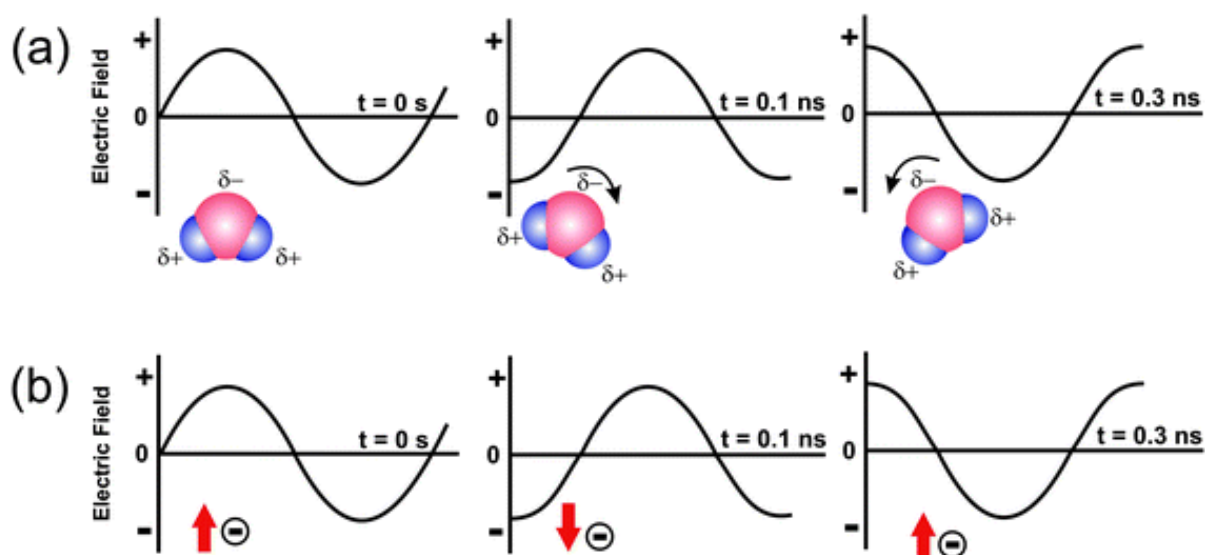


Figure 1.10 Two main heating mechanisms under microwave irradiation: (a) dipolar polarization; (b) ionic conduction mechanism.⁹³

Compared with traditional heating methods such as oil baths or mantle heating, which rely on surface-to-center thermal conduction and often suffer from temperature gradients. MW heating enables volumetric and uniform temperature distribution throughout the entire reaction medium. This leads to shorter reaction times, accelerated nucleation, and better control over particle size and morphology. Furthermore, MW-assisted synthesis allows selective heating in mixed systems and often eliminates the need for direct contact between the heat source and reactor.

Despite these significant benefits, MW-assisted synthesis also faces challenges, including equipment cost, limited penetration depth, and difficulty in scaling up for industrial production. Nevertheless, for laboratory-scale catalyst development, this method remains highly effective and efficient.

Hydrothermal/Solvothermal Method

The hydrothermal synthesis is a widely used method that involves crystallization of materials from aqueous solution under elevated temperatures and pressures in sealed autoclaves.^{94,95} When non-aqueous solvents are used, the process is termed

solvothermal synthesis. The key steps of hydrothermal crystal growth are as follows:

1. The reactants dissolve in the heated solution, dissociating into ions or forming molecular clusters.
2. Due to temperature differences between the top and bottom of the autoclave, these ions or molecular clusters migrate between different regions.
3. These species are transported to the lower-temperature region, where seed crystals are formed and an oversaturated solution is created.
4. The ions or molecular clusters adsorb onto the seed crystals, undergo decomposition, and desorb at the crystal growth interface, facilitating the movement of adsorbed species along the surface.
5. Finally, the dissolved substances crystallize onto the seeds, completing the crystal growth process.

Hydrothermal conditions can be finely tuned through temperature, pressure, reaction time, pH values, and additives, to control particle size, shape, crystallinity, and phase composition. Templates or surfactants may also be used to achieve desired surface textures or morphologies, which are crucial for maximizing active site exposure and mass/electron transport.^{96,97}

Furthermore, hydrothermal or solvothermal methods are widely used to grow nanomaterials onto conductive substrates, such as nickel foam, copper foam, carbon cloth, and carbon paper, thereby eliminating the process of preparation for catalyst ink and coating process. Moreover, the metal foams and carbon-based supports provide high conductivity and fast electron transfer, boosting the electrocatalytic efficiency.

Building upon the synthesis methods discussed above, the performance of electrocatalysts is not only determined by their basic composition and preparation techniques, but also strongly influenced by microstructure, electronic state distribution, and interfacial properties. To achieve high efficiency in electrocatalytic reactions, it is therefore essential to go beyond conventional synthesis and incorporate rational

structural design and surface/interface engineering to further optimize catalytic activity.

1.5.2 Catalyst Design and Regulation Strategies

In addition to synthesis methods, the rational design and precise regulation of electrocatalysts at the atomic, molecular, and mesoscale levels are equally critical to their overall performance. As displayed in [Figure 1.11](#), the electrocatalytic process mainly consists of multiple coupled and dynamic steps, including mass transfer and diffusion of reactants, adsorption-desorption of species, interfacial charge transfer, and surface-involved elementary reactions. These steps contribute to the formation of a real-time, multi-dimensional, and highly complex interfacial catalytic system.^{98–100} Therefore, optimizing and modifying the surface of the electrocatalyst is crucial for enhancing catalytic activity.

To the end, various strategies, such as size engineering, morphology control, heterointerface construction, heteroatom doping, and defect engineering, are used to optimize the catalyst's energy band structure, electrical conductivity, active site exposure, and electronic structure. The following sections highlight these key strategies.

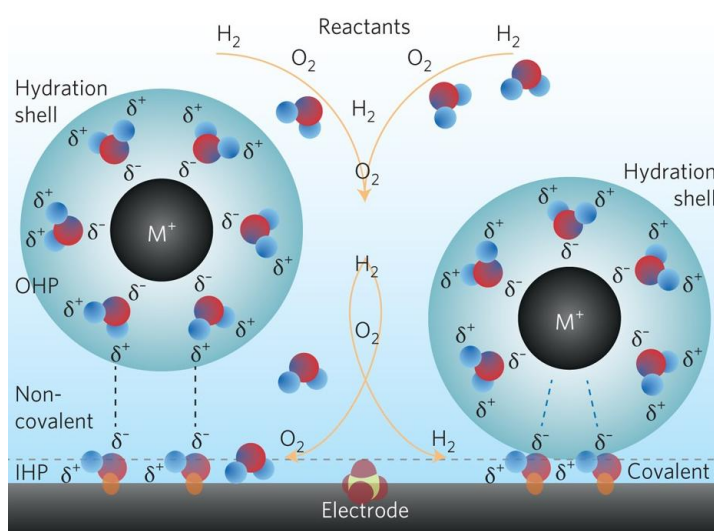


Figure 1.11 The electrochemical catalytic process on the catalyst's surface.⁹⁹

Size Engineering

In electrocatalysts, especially homogenous catalysts, the number of active atoms directly exposed to the electrolyte plays a crucial role in determining catalytic activity. Therefore, reducing catalyst particle size effectively increases the surface-to-volume ratio, thereby enhancing the density of exposed active sites and boosting catalytic activity.¹⁰¹ As shown in [Figure 1.12](#), as the size of metal nanoparticles decreases from clusters to individual atoms, notable changes occur in both their structural and electronic properties.¹⁰²

However, a major challenge associated with size reduction is the corresponding increase in surface free energy. Particularly in the case of SACs, the high surface free energy can lead to thermodynamic instability, resulting in atom migration and aggregation into larger nanoparticles ([Figure 1.12c](#)).¹⁰³ To address this issue, it is essential to anchor the single atoms onto suitable support materials, such as doped carbon frameworks, defective oxides, or metal-organic frameworks, which help stabilize the atomic dispersion and prevent aggregation, this is associated with the example for HER in **Section 1.4.1**.

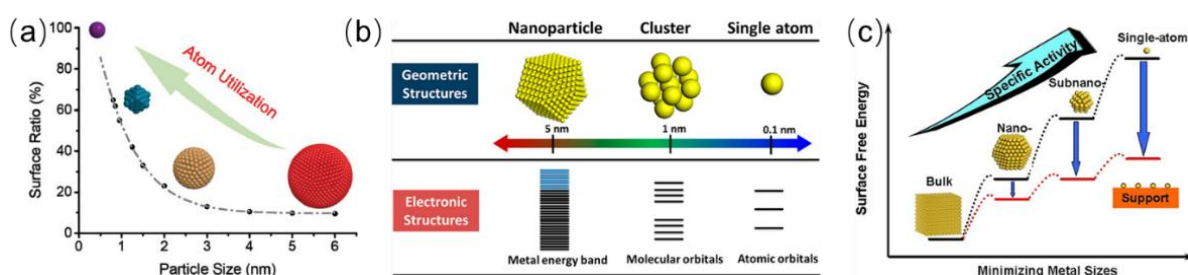


Figure 1.12 (a) Ratio of surface atoms as a function of particle sizes.¹⁰¹ (b) Geometric and electronic structures of single atoms, clusters, and nanoparticles.¹⁰² (c) Schematic illustration of the changes of surface free energy and specific activity per metal atom with metal particle size and the support effects on stabilizing single atoms.¹⁰²

This approach is especially important for precious metals like Pt, Ir, and Ru, where downsizing to the atomic scale not only achieves high catalytic activity but also enables maximal atom utilization. As a result, SACs enable significant reductions in precious

metal loading while maintaining excellent performance, offering both economic and sustainability benefits.

Morphology Control

While size reduction increases the proportion of active atoms, controlling the catalyst morphology further improves catalytic activity by tailoring surface area, electronic structure, and mass transport properties. Catalysts with similar chemical compositions but different morphologies can typically exhibit different surface areas, pore structures, and densities of accessible active sites, significantly altering catalytic behaviour.^{104–107}

To systematically classify morphologies, nanocatalysts are typically categorized into four dimensional types: 0D (e.g., nanodots), 1D (e.g., nanowires, nanotubes, nanorods), 2D (e.g., nanosheets, films), and 3D nanostructures (e.g., dendrimers),¹⁰⁸ as summarized in [Figure 1.13](#). Among these, low-dimensional materials (0-2D) are particularly notable. Due to confinement effects and anisotropic growth along specific lattice directions, they offer enhanced surface atom exposure and rapid electron transport pathways. These features render them highly effective for electrocatalytic applications.¹⁰⁹

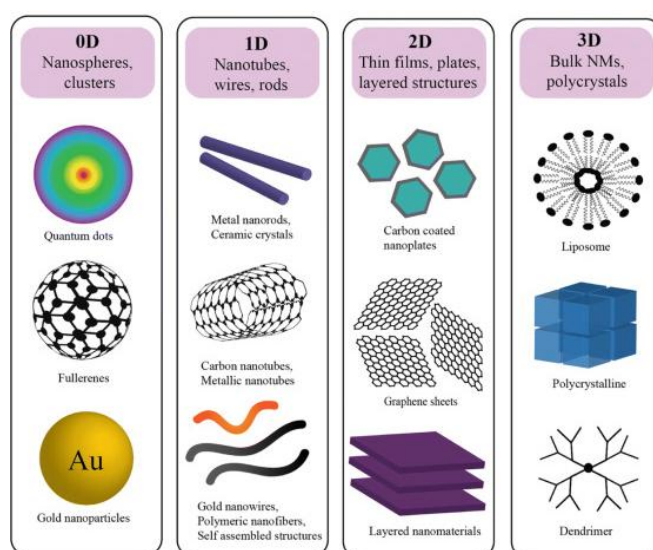


Figure 1.13 Representation of different types of nanostructures based on dimensions.¹¹⁰

However, it is important to note that lower dimensionality does not always guarantee better catalytic performance. Other physicochemical factors, such as surface wettability, porosity, and the interaction strength between the catalytic phase and the underlying substrate, also play decisive roles in determining overall efficiency. Therefore, optimizing morphologies is a complementary strategy that works synergistically with size engineering and other design approaches.

Heterointerface Construction

A heterointerface refers to the boundary formed between two different materials, as illustrated in [Figure 1.14](#). Due to the disruption of crystal symmetry at the interface, unique quantum states and special physical-chemical properties are distinct from the bulk material.¹¹¹ Importantly, the spontaneous formation of built-in electric fields at the heterointerfaces promotes charge transfer and induces local charge redistribution, thereby enhancing the catalyst's electrical conductivity.

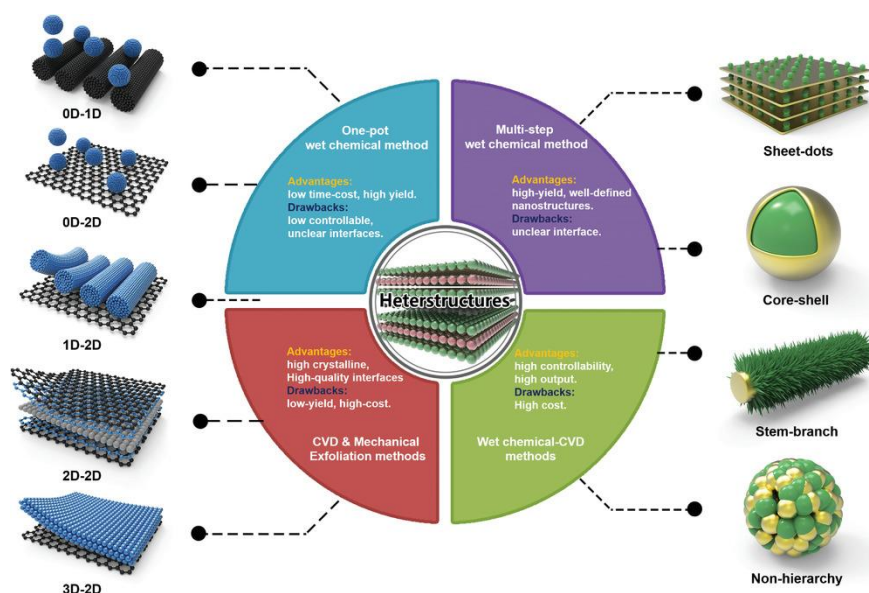


Figure 1.14 Schematic comparison of synthesis routes for heterostructures.¹¹²

More importantly, heterointerface engineering represents an effective strategy for

improving electrocatalytic activity by utilizing the synergistic effects between dual or multiple active sites at the interface.¹¹³ For example, the core-shell structure is a typical example of a heterostructure, where a shell layer encapsulates the core. This configuration enables uniform dispersion and enhanced stabilization of active sites. Moreover, strong interactions across the core-shell interface, whether electronic coupling or chemical bonding, further promote catalytic performance by tuning electronic properties and facilitating reaction kinetics.¹¹⁴

Heteroatom Doping

Heteroatom doping regulation involves embedding heteroatoms into the host material's crystal structure, thereby altering its physical-chemical properties, such as element composition and electronic structure.¹¹⁵ Normally, it can be categorized into single-, bi-, and tri-heteroatom doping, as shown in [Figure 1.15](#). This is one of the most widely used methods to improve catalytic performance.

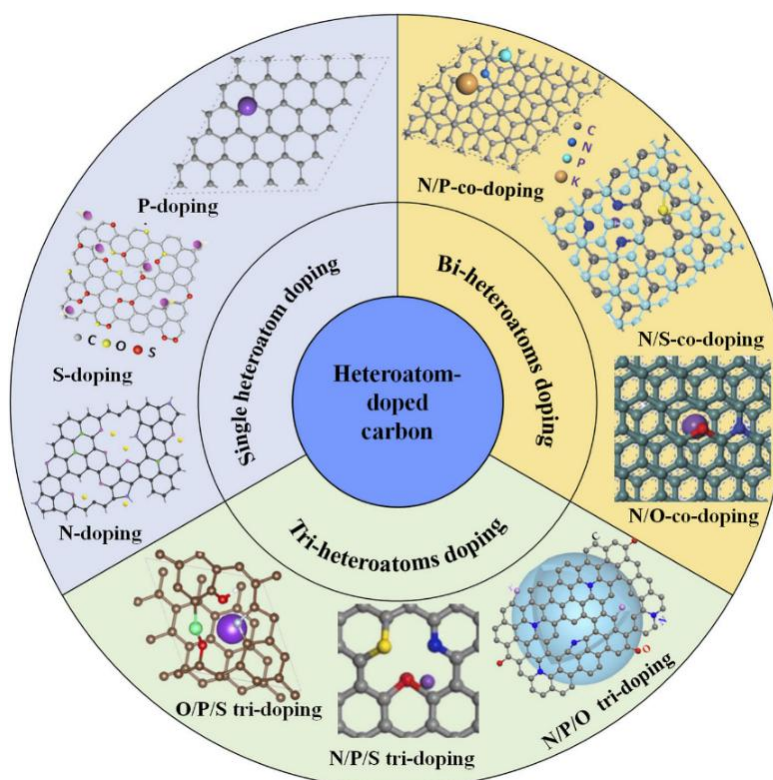


Figure 1.15 Schematic diagram of the different doping strategies.¹¹⁶

Doping can be further classified into cationic doping (substituting metal sites) and anionic doping (substituting non-metal sites). Due to differences in electronegativity, atomic radius, and valence states between dopant and host atoms, heteroatom doping modifies the electronic density and energy band structure, effectively tuning the adsorption strength of active sites for reactants.^{117,118}

Beyond electronic effects, heteroatom incorporation can induce lattice defects or distortions in the catalyst, altering the local coordination environment of active sites. The synergistic interaction among defect sites, active metal sites, and dopants can influence reaction pathways and dynamics, ultimately leading to improved electrocatalytic performance.¹¹⁹

Defect Engineering

Both experimental and computational studies have demonstrated that introducing defects into catalysts can promote the catalytic process through multiple mechanisms:¹²⁰

1. tuning the electronic structure to facilitate charge transfer
2. optimizing the active sites' density and distribution
3. enhancing electronic conductivity within the material

As a widely utilized strategy, defect engineering modulates both the structure and electronic properties of electrocatalysts to tailor their activity and stability.

Common defects include cationic (metal atoms) vacancies, anionic (non-metal atoms) vacancies, and mixed (both metal and non-metal sites) vacancies ([Figure 1.16a](#)). Compared to anionic vacancies, cationic vacancies have a higher formation energy, and thus most defect studies focus on anionic vacancies¹²¹. Among them, O_v are the most extensively studied and are known to enhance OER activity by modulating

intermediate adsorption energy and generating abundant active sites.

In addition to O_v , other anionic vacancies, such as sulfur, selenium, and phosphorus vacancies have been introduced to further tailor catalytic performance as shown in

Figure 1.16b.

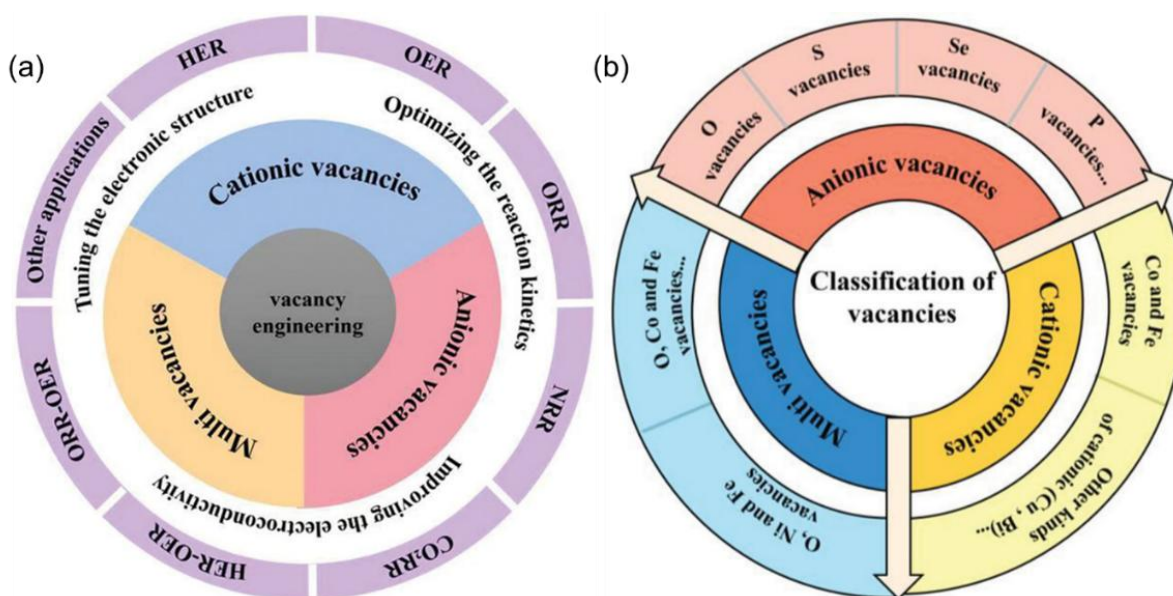


Figure 1.16 (a) Schematic diagram of the vacancy engineering, their properties and applications, (b) Schematic illustration of the classification of vacancies.¹²¹

1.6 Evaluation for Electrocatalysts

Building upon the previous discussions on the synthesis and structural design of electrocatalysts, it is essential to quantitatively evaluate their performance through systematic electrochemical tests. While synthetic strategies determine the structural and electronic features of catalysts, their ultimate effectiveness must be validated under relevant operating conditions.

In electrocatalytic reactions, the performance of the catalyst directly impacts reaction efficiency, energy consumption, and economic feasibility. Therefore, comprehensive evaluation of catalytic activity, selectivity, and stability under operating conditions is

crucial for practical application. Key performance metrics include geometric activity, specific activity, mass activity, and turnover frequency (TOF), which help assess the catalyst's reaction rate and efficiency. Furthermore, characterization methods such as Tafel slope, cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS) are widely used to probe reaction kinetics, charge transfer processes, and long-term stability.

Together, these evaluation strategies bridge the gap between catalyst design and real-world functionality, enabling both benchmark performance and mechanistic insights to guide further structural tuning.

Since electrocatalytic reactions occur at the surface/interface, the intrinsic electrocatalytic activity of a catalyst is most commonly defined as the several activity normalization metrics, as shown in [Figure 1.17](#), leading to the consideration of geometric activity, specific activity, and mass activity.

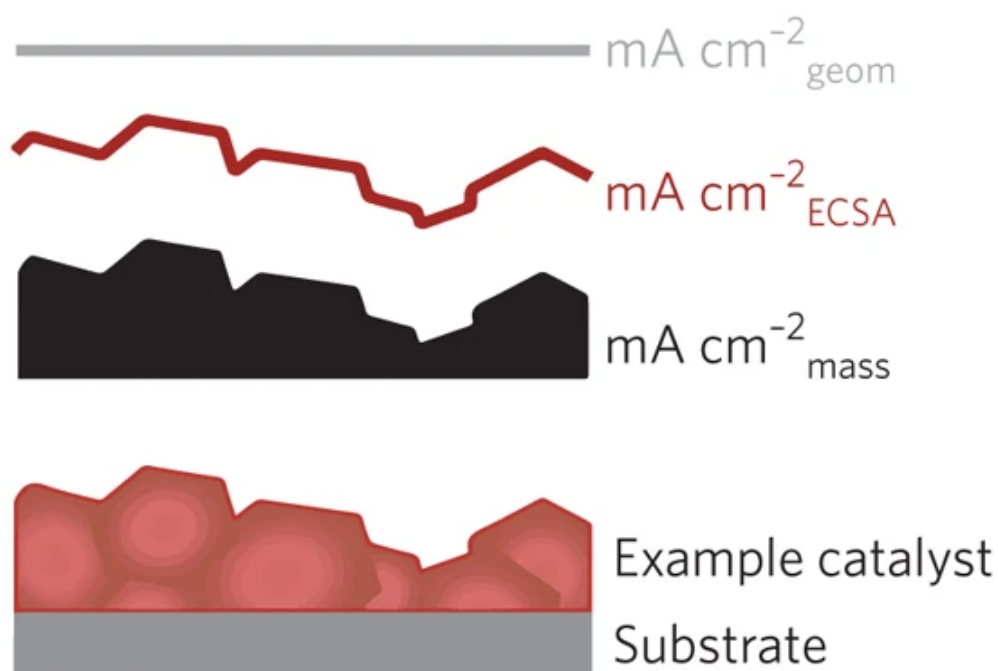


Figure 1.17 Illustration of a model catalyst surface highlighting differences between electrode geometric area, electrochemical surface area (ECSA), and catalyst mass loading. These diagrams demonstrate the importance of normalizing catalytic activity by surface area and active site density to accurately compare the intrinsic performance of different catalysts.³⁷

1.6.1 Geometric Activity ($\text{mA}\cdot\text{cm}^{-2}_{\text{geom}}$)

Geometric activity is one of the most commonly parameters for evaluating catalytic performance, particularly in early-stage screening or practical device testing. It is defined as the catalytic current normalized to the projected geometric area of the working electrode (WE), expressed in $\text{mA}\cdot\text{cm}^{-2}_{\text{geom}}$. However, geometric activity does not reflect the intrinsic activity, as it is significantly influenced by factors such as catalyst loading, distribution uniformity, film thickness and porosity of support. Within a specific loading range, the geometric activity tends to increase proportionally with the amount of loaded catalyst, potentially masking the actual catalytic efficiency per active site.

Under macro-electrolysis conditions, catalyst activity is typically assessed under a constant overpotential (η), where η represents the difference between the applied potential (E) and the theoretical equilibrium potential (E_0), given by $\eta=E-E_0$. Additionally, the internal resistance (R_s) within the electrocatalyst, solvent, electrochemical system, wiring, and equipment inevitably introduces an ohmic potential drop that needs to be compensated, as called iR compensation. Therefore, the voltage required to drive the electrochemical reaction is expressed as $E = E_0 + iR_s + \eta$, where iR_s is the ohmic voltage drop in the measurement system.

To benchmark and compare catalysts, key parameters include the onset potential, which is the potential corresponding to a low current density begins to appear, reflecting the catalyst's ability to initiate the reaction at minimal energy input. A lower onset potential, closer to the theoretical thermodynamic potential, indicates superior performance. Moreover, overpotential values at standardized current densities (j), such as 10, 100, and 1000 $\text{mA}\cdot\text{cm}^{-2}_{\text{geom}}$, are widely adopted to compare with other catalysts in publications.

1.6.2 Specific Activity ($\text{mA}\cdot\text{cm}^{-2}_{\text{ECSA}}$)

Specific activity is the catalytic current normalized to the electrochemical active surface

area (ECSA) of the WE, providing a more intrinsic calculation of catalyst performance that is theoretically independent of particle morphology or catalyst loading.³⁷ This metric enables a more accurate comparison of the inherent reactivity of different catalysts by accounting for the actual number of accessible active sites, which is different to the geometric activity.

In order to calculate the specific activity, it is essential to determine the ECSA, which is typically estimated via electrochemical techniques that quantify either Faradaic or non-Faradaic processes associated with the catalyst surface. Compared to geometric activity, specific activity more accurately reflects the intrinsic efficiency under working conditions. Generally, the ECSA of metal or metal oxide electrocatalysts is measured using two methods: Faradaic charge measurement and double-layer capacitance (C_{dl}).

Faradaic charge measurement: Faradaic charge measurement is a widely employed electrochemical technique to estimate the ECSA by quantifying the charge involved in specific surface-confined redox reactions.

A representative example is hydrogen underpotential deposition (H_{UPD}), where hydrogen atoms are adsorbed onto metal surfaces (typically Pt-based) at potentials above the equilibrium potential of hydrogen evolution, as shown in [Figure 1.18a](#). The associated desorption charge is directly proportional to the number of active Pt atoms, allowing for a reliable calculation of ECSA.

Another frequently used method is CO electrochemical stripping, where a monolayer of CO is first adsorbed onto the catalyst surface, followed by oxidative removal during an anodic scan. The charge passed during CO oxidation, as shown in [Figure 1.18b](#), correlates with the density of catalytic active sites, especially for systems where H_{UPD} is not applicable (e.g., alloyed or non-Pt catalysts).

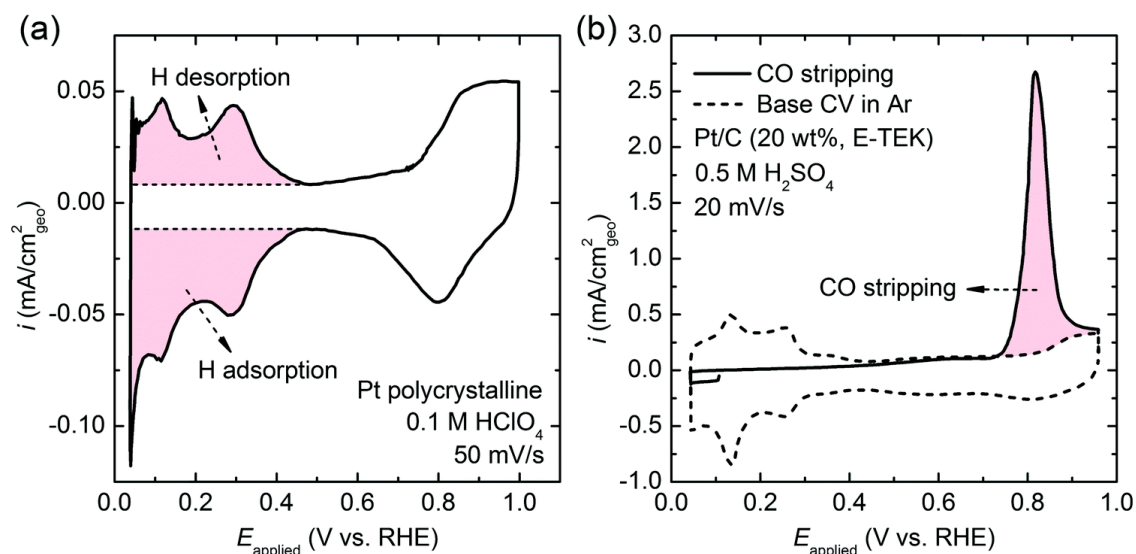


Figure 1.18 (a) Hydrogen adsorption/desorption for measuring the surface area of polycrystalline Pt at $50 \text{ mV}\cdot\text{s}^{-1}$ in Ar-saturated 0.1 M HClO_4 .¹²² (b) CO stripping quantifies the surface area of Pt/C at $20 \text{ mV}\cdot\text{s}^{-1}$ in Ar-saturated $0.5 \text{ M H}_2\text{SO}_4$.¹²³

In addition to Faradaic methods, the C_{dl} approach is also widely adopted. Below we summarize the detail:

Double-layer capacitance (C_{dl}): double-layer capacitance leverages the non-Faradaic charging current associated with the electrochemical double layer at the electrode/electrolyte interface. Since C_{dl} is proportional to the exposed surface area, it serves as an indirect but practical proxy for estimating ECSA. The relationship is given by:

$$\text{ECSA} = C_{dl}/C_s \quad \text{Eq.(16)}$$

where C_s represents the capacitance of a smooth, flat electrode surface under identical conditions.

While Faradaic methods offer higher accuracy in well-defined systems, C_{dl} measurements are more broadly applicable, especially for nanostructured or amorphous materials. Together, these techniques play a central role in normalizing catalytic current and assessing the intrinsic activity of electrocatalysts.

1.6.3 Mass Activity ($\text{mA} \cdot \text{mg}^{-1}_{\text{mass}}$)

Mass activity refers to the catalytic current normalized by the mass of the loaded active materials on WE, and is particularly crucial for evaluating noble-metal-based catalysts (e.g., Pt, Pd, RuO₂, IrO₂, et al.), where metal utilization directly impacts overall cost. For a given catalyst loading, smaller particle sizes tend to exhibit higher mass activity due to their larger specific surface area, which enhances active site accessibility. Consequently, mass activity is strongly influenced by the dispersion and morphology of the active materials. To optimize cost efficiency for commercial applications, strategies such as reducing metal loading or improving metal dispersion by forming nano-clusters or single-atom structures are essential.

In addition to these three methods for calculating different types of activity, there are several key parameters that can be used to assess the catalyst's performance and intrinsic mechanisms from different perspectives, including turnover frequency (TOF), Tafel slope, electrochemical impedance spectroscopy (EIS), and stability.

1.6.4 Turnover Frequency (TOF)

The TOF provides a direct measure of the intrinsic catalytic activity by quantifying the number of product molecules generated per active site per unit time.¹²⁴ It is particularly valuable for comparing catalysts with different surface areas or morphologies, as it normalizes activity to the number of catalytically active centers rather than the total catalyst mass.

The TOF can be expressed as:

$$\text{TOF} = I / (\alpha \cdot n \cdot F) \quad \text{Eq. (17)}$$

where I is the catalytic current (A), α is the number of electrons transferred in the reaction, F is Faraday's constant ($96485 \text{ C} \cdot \text{mol}^{-1}$), and n is the number of active sites (mol).

A major challenge in accurately quantifying TOF is the dynamic nature of catalyst surfaces during electrocatalytic reactions. Surface reconstruction and morphological evolutions often alter the number of active sites in real time. These effects complicate reliable quantification and require careful experimental calibration, such as combining electrochemical measurements with ex-situ or operando characterization techniques to monitor changes in surface chemistry.

1.6.5 Tafel Slope

To better understand the electrocatalytic kinetics of a given catalyst, the Tafel plot is a widely employed analytical tool. By plotting the overpotential (η) against the logarithm of the current density ($\log j$), it illustrates how the reaction rate varies with the applied potential, particularly in the kinetically controlled region where charge transfer dominates. The resulting linear relationship enables interpretation of reaction kinetics and provides mechanistic insights.

The slope of this plot, known as the Tafel slope, is an intrinsic property of the catalyst that reflects the relationship between η and the catalytic current density (j), as described by the Butler-Volmer equation¹²⁵:

$$|\eta| = (2.3RT)/(\alpha nF) \cdot \log(j / j_0) \quad \text{Eq. (18)}$$

where R and F are constants representing the ideal gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{C}^{-1}$) and Faraday's constant ($96485 \text{ C} \cdot \text{mol}^{-1}$), respectively. T is the absolute temperature in Kelvin, α is the electrochemical transfer coefficient, n is the number of transferred electrons, j is the catalytic current density, and j_0 is the exchange current density.

Accordingly, the Tafel slope (b , $\text{mV} \cdot \text{dec}^{-1}$) is given by:

$$b = (2.3RT)/(\alpha nF) \quad \text{Eq. (19)}$$

The Tafel slope, obtained by fitting the linear portion of the Tafel plot, provides insight into the rate-determining step and reflects the charge transfer kinetics of the

electrocatalytic process. A lower Tafel slope implies that a smaller overpotential is needed to reach a certain current density, indicating faster reaction kinetics and better catalytic performance. Hence, Tafel analysis is essential for comparing the kinetic efficiencies of electrocatalysts.

1.6.6 Electrochemical Impedance Spectroscopy (EIS)

Typical electrochemical processes involve multiple fundamental components, including charge transfer, mass transport, and double-layer capacitance. EIS is a powerful analytical technique able to evaluate this processes by applying small amplitude alternating current (AC) across a range of frequencies and measuring the system's response.¹²⁶

The EIS spectrum is typically divided into high- and low-frequency regions. In the high-frequency region, the response is dominated by primarily by charge transfer process, where a characteristic semicircle appears in the Nyquist plot, representing the charge transfer resistance (R_{ct}). A smaller semicircle radius indicates a faster electron transfer rate at the electrode/electrolyte interface. In contrast, the low-frequency region is controlled mainly by mass transfer phenomena, such as diffusion of reactants and intermediates within the electrolyte.

To quantitatively interpret EIS data, equivalent circuit models are commonly employed to simulate the electrochemical behavior of the electrode/electrolyte interface. The most widely used model is the Randles circuit, which typically includes the solution resistance (R_s), C_{dl} , R_{ct} , and a Warburg impedance element (Z_w) to represent ion diffusion. By fitting experimental impedance data to this equivalent circuit, one can extract key kinetic and transport parameters such as R_{ct} and C_{dl} , enabling detailed analysis of catalytic activity, electron transfer efficiency, and diffusion limitations.

For more complex systems, such as porous electrodes or multistep reactions, the

Randles model can be modified or extended to better capture the behavior of multiple time constants and interfaces. Overall, EIS serves as a crucial tool in understanding and optimizing charge transport, reaction kinetics, and mass transfer phenomena in electrocatalytic systems.

1.6.7 Catalytic Stability

Catalyst stability is a crucial factor for evaluating whether a catalyst can be practically used, particularly in harsh environments such as acidic proton-exchange membrane water electrolysis (PEMWE) and direct seawater electrolysis technologies. In the PEMWE system, the strong oxidizing and corrosive environment often causes catalyst reconstruction and collapse, leading to aggregation or loss of the active sites. Similarly, in seawater electrolysis, the presence of alkaline earth metal ions (Ca^{2+} , Mg^{2+} , Ba^{2+}) and halide ions (Cl^- , Br^- , etc.) results in the formation of insulating alkaline earth metal hydroxide precipitates on the catalyst surface, covering the active sites and causing catalyst deactivation.

To assess the long-term durability and structural robustness of electrocatalysts, two main evaluation methods are commonly employed:

1. Steady-state testing: includes chronoamperometry (constant potential) and chronopotentiometry (constant current) to assess long-term catalytic performance and durability.
2. Transient testing: employs cyclic voltammetry and square wave voltammetry to investigate changes in catalyst durability and structural stability over time.

Combining these methods provides a comprehensive understanding of catalyst stability under realistic operating conditions, which is essential for the design of durable electrocatalysts in practical applications.

1.7 Thesis Objectives and Framework

As already summarized above, water electrolysis technology for green hydrogen production plays a crucial role in modern energy conversion and storage engineering. Electrocatalysts, as a core component of this process, have been extensively studied in both academia and industry. Since the water electrolysis reactions (HER and OER) are typical surface-interface-driven processes, the rational design and precise synthesis of catalysts with abundant exposed active sites are essential for improving overall electrolysis efficiency and long-term stability. On these grounds, the study and development of novel synthetic approaches capable of controlling the morphological, compositional, and structural features of electrocatalysts is of great interest.

1.7.1 Thesis Objectives

Building upon the robust foundation established by the Group of Nanoparticles and Nanocomponents (NN Group) in MW-assisted synthesis of functional nanocrystals, such as iron oxide,^{127,128} gold,^{129–131} and copper oxide,¹³² this thesis aims to further advance the development of electrocatalyst for sustainable hydrogen production. The primary focus is to enhance the electrocatalytic efficiency of the cathodic HER (**Obj.1**) and improve the performance and long-term stability of the anodic OER (**Obj.2**), particularly in challenging environments such as natural seawater, where corrosion and ion interference can significantly impair performance.

To further address the limitations of sluggish OER kinetics and high overpotential, the thesis also explores alternative anodic reactions, such as EOR, as a replacement for the conventional OER (**Obj.3**). By employing EOR as a coupled reaction, the overall energy input required for hydrogen production can be significantly reduced, while simultaneously generating value-added chemical products.

Leveraging our group's strengths in structure to property relationship, heterostructure

design, and advanced nanomaterial characterization, we systematically design and synthesize promising catalyst systems. Synthetic strategies including morphology and structure control, defect engineering, heteroatom doping, and interfacial modulation are employed to tailor the electronic structure, active site exposure, and reaction kinetics of novel electrocatalysts. These efforts are directed toward enhancing intrinsic activity, improving stability under operational conditions, and minimizing reliance on noble metals. Ultimately, this research aims to contribute to the deployment of efficient, durable, and cost-effective electrocatalysts for the large-scale industrial production of green hydrogen.

1.7.2 Thesis Framework

To address the challenges including high overpotentials, catalyst degradation, and limited noble metal resources, three representative electrocatalyst systems are investigated:

I. AuPt Core-shell Nanocrystals for HER via MW-assisted Synthesis (Obj.1)

A series of AuPt NCs were synthesized using a MW-assisted method, where chloride ions directed Au atoms nucleation while guiding Pt atoms to the surface to form a uniform shell. This architecture maximized Pt exposure for catalytic activity, while the Au core enhanced electron conductivity and HER kinetics. By systematically tuning the Au/Pt precursor ratio, chloride ion concentration, PVP dosage, and reaction time, precise control over particle size and morphology was achieved. The optimal AuPt core-shell nanocatalyst ($\text{AuPt}_{1/4\text{Cl}}$) exhibited outstanding HER activity, achieving an overpotential of only 24 mV at $10 \text{ mA}\cdot\text{cm}^{-2}$, with a remarkable low Tafel slope of $13 \text{ mV}\cdot\text{dec}^{-1}$. Furthermore, the mass activity reached $13.8 \text{ A}\cdot\text{mg}^{-1}_{\text{Pt}}$, approximately 6.9 times higher than that of commercial Pt/C, indicating a significant Pt utilization efficiency. These findings highlight that structural engineering and MW-assisted

structural engineering in enhancing HER catalytic performance while reducing noble metal usage, making this approach highly promising for scalable hydrogen production.

II. B and Al Doped NiFe LDH for OER via Hydrothermal and Reduction Treatment (Obj.2)

NiFe LDH were co-doped with Al and B via hydrothermal synthesis and subsequent NaBH_4 reduction, introducing both heteroatoms and oxygen vacancies (O_v). Al served as a structural bridge within the LDH lattice, while B incorporation formed strong metal-boron (M-B) bonds (Ni-B, Fe-B, Al-B), enhancing electronic conductivity and mechanical robustness. The resulting B,Al-NiFe LDH exhibited remarkable OER activity in alkaline electrolytes, requiring overpotentials of 169, 196, and 254 mV to achieve current densities of 10, 100, and $500 \text{ mA}\cdot\text{cm}^{-2}$, respectively, with a Tafel slope of $38.6 \text{ mV}\cdot\text{dec}^{-1}$. The ECSA reached 254.50 cm^2 and TOF was 2.05 s^{-1} . In natural seawater electrolysis, the catalyst delivered a low overpotential of 250 mV at $100 \text{ mA}\cdot\text{cm}^{-2}$. When paired with Pt/C for full water splitting, it achieved a voltage reduction of 400 mV compared to a benchmark $\text{RuO}_2\|\text{Pt}/\text{C}$ system at $400 \text{ mA}\cdot\text{cm}^{-2}$. Combined experimental and DFT analyses revealed that B and Al co-doping modulates the oxidation states of Ni and Fe, promotes lattice oxygen participation, and lowers the energy barrier for O-O coupling via an enhanced LOM. These findings underscore the potential of boron-based defect engineering in advancing seawater-compatible OER catalysts.

III. Cu/CoO Core-shell Heterostructures for Alcohol Oxidation Reaction via MW-assisted Method (Obj.3)

To address the limited value of anodic evolution in conventional electrolysis, this work explores AOR as alternatives. Cu-core/CoO-shell heterostructures were synthesized using a MW-assisted method by exploiting the redox potential difference between Cu and Co. The resulting architecture featured strong electronic coupling at the core-shell

interface, promoting efficient charge transfer and catalyst stability. Compared to the conventional OER process, the $\text{CuCo}_{2/1}$ core-shell catalyst reduced the required overpotentials by 155 mV for MOR and 197 mV for EOR at $50 \text{ mA}\cdot\text{cm}^{-2}$. Unlike traditional Pt- and Pd-based catalysts, which fully oxidize methanol or ethanol to CO_2 or CO, $\text{CuCo}_{2/1}$ selectively produced value-added formic acid (from methanol) and acetic acid (from ethanol). Moreover, in a hybrid ethanol-water electrolysis system, $\text{CuCo}_{2/1}\|\text{Pt}/\text{C}$ achieved $400 \text{ mA}\cdot\text{cm}^{-2}$ at only 1.91 and 2.00 V for ethanol and methanol oxidation, respectively, significantly lower than the 2.27 V required for conventional water splitting. This demonstrates a dual benefit strategy, improving hydrogen production efficiency while generating high-value liquid chemicals.

In summary, these three catalyst systems address the three main objective of the thesis, showcasing how atomic-level design strategies effectively tackle key challenges in water electrolysis, including slow kinetics, low stability, and reliance on noble metals. This thesis lays the groundwork for the future development of advanced electrocatalysts and offers scalable pathways for the implementation of sustainable hydrogen production technologies.

1.8 References

- 1 Chu, S.; Majumdar, A. Opportunities and challenges for a sustainable energy future. *Nature* **2012**, *488* (7411), 294-303. <https://doi.org/10.1038/nature11475>.
- 2 Jacobson, M. Z.; Delucchi, M. A.; Cameron, M. A.; Coughlin, S. J.; Hay, C. A.; Manogaran, I. P.; Shu, Y.; Von Krauland, A.-K. Impacts of green new deal energy plans on grid stability, costs, jobs, health, and climate in 143 countries. *One Earth* **2019**, *1* (4), 449-463. <https://doi.org/10.1016/j.oneear.2019.12.003>.
- 3 Martins, F.; Felgueiras, C.; Smitskova, M.; Caetano, N. Analysis of fossil fuel energy consumption and environmental impacts in European countries. *Energies* **2019**, *12* (6), 964. <https://doi.org/10.3390/en12060964>.
- 4 Lott, M. C.; Pye, S.; Dodds, P. E. Quantifying the co-impacts of energy sector decarbonisation on outdoor air pollution in the United Kingdom. *Energy Policy* **2016**, *101*, 42-51. <https://doi.org/10.1016/j.enpol.2016.11.028>.
- 5 Sugiawan, Y.; Managi, S. New evidence of energy-growth nexus from inclusive wealth. *Renewable and Sustainable Energy Reviews* **2018**, *103*, 40-48. <https://doi.org/10.1016/j.rser.2018.12.044>.
- 6 Jacobson, M. Z.; Delucchi, M. A.; Bauer, Z. A. F.; Goodman, S. C.; Chapman, W. E.; Cameron, M. A.; et al. 100% Clean and renewable wind, water, and sunlight all-sector energy roadmaps for 139 countries of the world. *Joule* **2017**, *1* (1), 108-121. <https://doi.org/10.1016/j.joule.2017.07.005>.
- 7 Pathak, P. K.; Yadav, A. K.; Padmanaban, S. Transition toward emission-free energy systems by 2050: potential role of hydrogen. *International Journal of Hydrogen Energy* **2022**, *48* (26), 9921-9927. <https://doi.org/10.1016/j.ijhydene.2022.12.058>.
- 8 Westphal, I. The effects of reducing renewable power intermittency through portfolio diversification. *Renewable and Sustainable Energy Reviews* **2024**, *197*, 114415. <https://doi.org/10.1016/j.rser.2024.114415>.
- 9 Giovanni, D. C.; Maroufi, S. M.; Beiranvand, H.; Valerio, D. A.; D'Arco, S.; Gevorgian, V.; Waczowicz, S.; Mather, B.; Liserre, M.; Hagenmeyer, V. The role of energy storage systems for a secure energy supply: a comprehensive review of system needs and technology solutions. *Electric Power Systems Research* **2024**, *236*, 110963. <https://doi.org/10.1016/j.epsr.2024.110963>.
- 10 Hassan, Q.; Algburi, S.; Sameen, A. Z.; Salman, H. M.; Jaszczur, M. A review of hybrid renewable energy systems: solar and wind-powered solutions: challenges, opportunities, and policy implications. *Results in Engineering* **2023**, *20*, 101621. <https://doi.org/10.1016/j.rineng.2023.101621>.
- 11 Gao, M.; Sheng, W.; Zhuang, Z.; Fang, Q.; Gu, S.; Jiang, J.; Yan, Y. Efficient water oxidation using nanostructured a-nickel-hydroxide as an electrocatalyst. *Journal of the American Chemical Society* **2014**, *136* (19), 7077-7084. <https://doi.org/10.1021/ja502128j>.
- 12 Nkinyam, C. M.; Ujah, C. O.; Asadu, C. O.; Kallon, D. V. V. Exploring geothermal energy as a sustainable source of energy: a systemic review. *Unconventional Resources* **2025**, *6*, 100149. <https://doi.org/10.1016/j.unres.2025.100149>.
- 13 Andersson, J.; Grönkvist, S. Large-scale storage of hydrogen. *International Journal of Hydrogen Energy* **2019**, *44* (23), 11901-11919. <https://doi.org/10.1016/j.ijhydene.2019.03.063>.
- 14 Vezzoni, R. Green growth for whom, how and why? The REPowerEU Plan and the inconsistencies of European Union energy policy. *Energy Research & Social Science* **2023**, *101*, 103134. <https://doi.org/10.1016/j.erss.2023.103134>.

- 15 Bhuiyan, M. M. H.; Siddique, Z. Hydrogen as an alternative fuel: a comprehensive review of challenges and opportunities in production, storage, and transportation. *International Journal of Hydrogen Energy* **2025**, *102*, 1026-1044. <https://doi.org/10.1016/j.ijhydene.2025.01.033>.
- 16 Zou, X.; Zhang, Y. Noble metal-free hydrogen evolution catalysts for water splitting. *Chemical Society Reviews* **2015**, *44* (15), 5148-5180. <https://doi.org/10.1039/c4cs00448e>.
- 17 Cook, T. R.; Dogutan, D. K.; Reece, S. Y.; Surendranath, Y.; Teets, T. S.; Nocera, D. G. Solar energy supply and storage for the legacy and nonlegacy worlds. *Chemical Reviews* **2010**, *110* (11), 6474-6502. <https://doi.org/10.1021/cr100246c>.
- 18 Grätzel, M. Photoelectrochemical cells. *Nature* **2001**, *414* (6861), 338-344. <https://doi.org/10.1038/35104607>.
- 19 Cai, Z.; Bu, X.; Wang, P.; Ho, J. C.; Yang, J.; Wang, X. Recent advances in layered double hydroxide electrocatalysts for the oxygen evolution reaction. *Journal of Materials Chemistry A* **2019**, *7* (10), 5069-5089. <https://doi.org/10.1039/c8ta11273h>.
- 20 Carapellucci, R.; Giordano, L. Steam, dry and autothermal methane reforming for hydrogen production: a thermodynamic equilibrium analysis. *Journal of Power Sources* **2020**, *469*, 228391. <https://doi.org/10.1016/j.jpowsour.2020.228391>.
- 21 Midilli, A.; Kucuk, H.; Topal, M. E.; Akbulut, U.; Dincer, I. A comprehensive review on hydrogen production from coal gasification: challenges and opportunities. *International Journal of Hydrogen Energy* **2021**, *46* (50), 25385-25412. <https://doi.org/10.1016/j.ijhydene.2021.05.088>.
- 22 Ranjekar, A. M.; Yadav, G. D. Steam reforming of methanol for hydrogen production: a critical analysis of catalysis, processes, and scope. *Industrial & Engineering Chemistry Research* **2021**, *60* (1), 89-113. <https://doi.org/10.1021/acs.iecr.0c05041>.
- 23 Li, D.; Xu, F.; Tang, X.; Dai, S.; Pu, T.; Liu, X.; Tian, P.; Xuan, F.; Xu, Z.; Wachs, I. E.; Zhu, M. Induced activation of the commercial Cu/ZnO/Al₂O₃ catalyst for the steam reforming of methanol. *Nature Catalysis* **2022**, *5* (2), 99-108. <https://doi.org/10.1038/s41929-021-00729-4>.
- 24 Li, X.-P.; Huang, C.; Han, W.-K.; Ouyang, T.; Liu, Z.-Q. Transition metal-based electrocatalysts for overall water splitting. *Chinese Chemical Letters* **2021**, *32* (9), 2597-2616. <https://doi.org/10.1016/j.ccllet.2021.01.047>.
- 25 Zhang, J.; Hu, C.; Deng, P.; Yin, Y. A review on synthesis and modification of cobalt-molybdenum based sulfides as hydrogen and oxygen evolution catalysts for water electrolysis. *Chemistry of Inorganic Materials* **2024**, *3*, 100043. <https://doi.org/10.1016/j.cinorg.2024.100043>.
- 26 Qiao, M.; Li, B.; Fei, T.; Xue, M.; Yao, T.; Tang, Q.; Zhu, D. Design strategies towards advanced hydrogen evolution reaction electrocatalysts at large current densities. *Chemistry - a European Journal* **2024**, *30* (20), e202303826. <https://doi.org/10.1002/chem.202303826>.
- 27 Skúlason, E.; Tripkovic, V.; Björketun, M. E.; Gudmundsdóttir, S.; Karlberg, G.; Rossmeisl, J.; Bligaard, T.; Jónsson, H.; Nørskov, J. K. Modeling the electrochemical hydrogen oxidation and evolution reactions on the basis of density functional theory calculations. *The Journal of Physical Chemistry C* **2010**, *114* (50), 22374. <https://doi.org/10.1021/jp110913n>.
- 28 Sheng, W.; Myint, M.; Chen, J. G.; Yan, Y. Correlating the hydrogen evolution reaction activity in alkaline electrolytes with the hydrogen binding energy on monometallic surfaces. *Energy & Environmental Science* **2013**, *6* (5), 1509. <https://doi.org/10.1039/c3ee00045a>.
- 29 Han, W.; Li, M.; Ma, Y.; Yang, J. Cobalt-based metal-organic frameworks and their derivatives for hydrogen evolution reaction. *Frontiers in Chemistry* **2020**, *8*, 592915. <https://doi.org/10.3389/fchem.2020.592915>.
- 30 Wang, X.; Zhong, H.; Xi, S.; Lee, W. S. V.; Xue, J. Understanding of oxygen redox in the oxygen evolution reaction. *Advanced Materials* **2022**, *34* (50), 2107956.

<https://doi.org/10.1002/adma.202107956>.

- 31 Xiang, R.; Peng, L.; Wei, Z. Tuning interfacial structures for better catalysis of water electrolysis. *Chemistry - a European Journal* **2019**, *25* (42), 9799-9815. <https://doi.org/10.1002/chem.201901168>.
- 32 Chen, S.; Wang, Y.; Wang, Z.; Zhang, K. Advances in nonprecious metal catalysts for efficient water oxidation in alkaline media. *Ionics* **2022**, *29* (1), 9-32. <https://doi.org/10.1007/s11581-022-04774-2>.
- 33 Galyamin, D.; Torrero, J.; Rodríguez, I.; Kolb, M. J.; Ferrer, P.; Pascual, L.; et al. Active and durable R_2MnRuO_7 pyrochlores with low Ru content for acidic oxygen evolution. *Nature Communications* **2023**, *14* (1), 2010. <https://doi.org/10.1038/s41467-023-37665-9>.
- 34 He, Y.; Kang, Z.; Li, J.; Li, Y.; Tian, X. Recent progress of manganese dioxide based electrocatalysts for the oxygen evolution reaction. *Industrial Chemistry and Materials* **2023**, *1* (3), 312-331. <https://doi.org/10.1039/d3im00034f>.
- 35 Wang, X.; Xi, S.; Huang, P.; Du, Y.; Zhong, H.; Wang, Q.; Borgna, A.; Zhang, Y.-W.; Wang, Z.; Wang, H.; Yu, Z. G.; Lee, W. S. V.; Xue, J. Pivotal role of reversible NiO_6 geometric conversion in oxygen evolution. *Nature* **2022**, *611* (7937), 702-708. <https://doi.org/10.1038/s41586-022-05296-7>.
- 36 Zhang, J.; Yang, H. B.; Zhou, D.; Liu, B. Adsorption energy in oxygen electrocatalysis. *Chemical Reviews* **2022**, *122* (23), 17028-17072. <https://doi.org/10.1021/acs.chemrev.1c01003>.
- 37 Montoya, J. H.; Seitz, L. C.; Chakthranont, P.; Vojvodic, A.; Jaramillo, T. F.; Nørskov, J. K. Materials for solar fuels and chemicals. *Nature Materials* **2016**, *16* (1), 70-81. <https://doi.org/10.1038/nmat4778>.
- 38 Man, I. C.; Su, H.; Calle-Vallejo, F.; Hansen, H. A.; Martínez, J. I.; Inoglu, N. G.; Kitchin, J.; Jaramillo, T. F.; Nørskov, J. K.; Rossmeisl, J. Universality in oxygen evolution Electrocatalysis on oxide surfaces. *ChemCatChem* **2011**, *3* (7), 1159-1165. <https://doi.org/10.1002/cctc.201000397>.
- 39 Song, J.; Wei, C.; Huang, Z.-F.; Liu, C.; Zeng, L.; Wang, X.; Xu, Z. J. A review on fundamentals for designing oxygen evolution electrocatalysts. *Chemical Society Reviews* **2020**, *49* (7), 2196-2214. <https://doi.org/10.1039/c9cs00607a>.
- 40 Zhang, N.; Chai, Y. Lattice oxygen redox chemistry in solid-state electrocatalysts for water oxidation. *Energy & Environmental Science* **2021**, *14* (9), 4647-4671. <https://doi.org/10.1039/d1ee01277k>.
- 41 Tomar, A. K.; Pan, U. N.; Kim, N. H.; Lee, J. H. Enabling lattice oxygen participation in a triple perovskite oxide electrocatalyst for the oxygen evolution reaction. *ACS Energy Letters* **2022**, *8* (1), 565-573. <https://doi.org/10.1021/acsenergylett.2c02617>.
- 42 Yang, H.; Li, F.; Zhan, S.; Liu, Y.; Li, W.; Meng, Q.; Kravchenko, A.; Liu, T.; Yang, Y.; Fang, Y.; Wang, L.; Guan, J.; Furó, I.; Ahlquist, M. S. G.; Sun, L. Intramolecular hydroxyl nucleophilic attack pathway by a polymeric water oxidation catalyst with single cobalt sites. *Nature Catalysis* **2022**, *5* (5), 414-429. <https://doi.org/10.1038/s41929-022-00783-6>.
- 43 Yang, C.; Fontaine, O.; Tarascon, J.; Grimaud, A. Chemical recognition of active oxygen species on the surface of oxygen evolution reaction electrocatalysts. *Angewandte Chemie International Edition* **2017**, *56* (30), 8652-8656. <https://doi.org/10.1002/anie.201701984>.
- 44 Lin, C.; Li, J.-L.; Li, X.; Yang, S.; Luo, W.; Zhang, Y.; Kim, S.-H.; Kim, D.-H.; Shinde, S. S.; Li, Y.-F.; Liu, Z.-P.; Jiang, Z.; Lee, J.-H. In-situ reconstructed Ru atom array on $\alpha\text{-MnO}_2$ with enhanced performance for acidic water oxidation. *Nature Catalysis* **2021**, *4* (12), 1012-1023. <https://doi.org/10.1038/s41929-021-00703-0>.

- 45 Hu, C.; Yue, K.; Han, J.; Liu, X.; Liu, L.; Liu, Q.; Kong, Q.; Pao, C.-W.; Hu, Z.; Suenaga, K.; Su, D.; Zhang, Q.; Wang, X.; Tan, Y.; Huang, X. Misoriented high-entropy iridium ruthenium oxide for acidic water splitting. *Science Advances* **2023**, *9* (37), eadf9144. <https://doi.org/10.1126/sciadv.adf9144>.
- 46 Jin, J.; Yin, J.; Hu, Y.; Zheng, Y.; Liu, H.; Wang, X.; Xi, P.; Yan, C. Stabilizing sulfur sites in tetraoxygen tetrahedral coordination structure for efficient electrochemical water oxidation. *Angewandte Chemie International Edition* **2023**, *63* (9), e202313185. <https://doi.org/10.1002/anie.202313185>.
- 47 You, B.; Liu, X.; Jiang, N.; Sun, Y. A General strategy for decoupled hydrogen production from water splitting by integrating oxidative biomass valorization. *Journal of the American Chemical Society* **2016**, *138* (41), 13639-13646. <https://doi.org/10.1021/jacs.6b07127>.
- 48 Ding, Y.; Miao, B.-Q.; Li, S.-N.; Jiang, Y.-C.; Liu, Y.-Y.; Yao, H.-C.; Chen, Y. Benzylamine oxidation boosted electrochemical water-splitting: Hydrogen and benzonitrile co-production at ultra-thin Ni₂P nanomeshes grown on nickel foam. *Applied Catalysis B: Environment and Energy* **2019**, *268*, 118393. <https://doi.org/10.1016/j.apcatb.2019.118393>.
- 49 Qian, Q.; Zhu, Y.; Ahmad, N.; Feng, Y.; Zhang, H.; Cheng, M.; Liu, H.; Xiao, C.; Zhang, G.; Xie, Y. Recent advancements in electrochemical hydrogen production via hybrid water splitting. *Advanced Materials* **2023**, *36* (4), 2306108. <https://doi.org/10.1002/adma.202306108>.
- 50 Deng, X.; Kang, X.; Li, M.; Xiang, K.; Wang, C.; Guo, Z.; Zhang, J.; Fu, X.-Z.; Luo, J.-L. Coupling efficient biomass upgrading with H₂ production via bifunctional Cu_xS@NiCo-LDH core-shell nanoarray electrocatalysts. *Journal of Materials Chemistry A* **2019**, *8* (3), 1138-1146. <https://doi.org/10.1039/c9ta06917h>.
- 51 Miao, J.; Teng, X.; Zhang, R.; Guo, P.; Chen, Y.; Zhou, X.; Wang, H.; Sun, X.; Zhang, L. "Carbohydrate-universal" electrolyzer for energy-saving hydrogen production with Co₃FeP_x@NF as bifunctional electrocatalysts. *Applied Catalysis B: Environment and Energy* **2019**, *263*, 118109. <https://doi.org/10.1016/j.apcatb.2019.118109>.
- 52 Lu, Y.; Dong, C.; Huang, Y.; Zou, Y.; Liu, Z.; Liu, Y.; Li, Y.; He, N.; Shi, J.; Wang, S. Identifying the geometric site dependence of spinel oxides for the electrooxidation of 5-hydroxymethylfurfural. *Angewandte Chemie International Edition* **2020**, *59* (43), 19215-19221. <https://doi.org/10.1002/anie.202007767>.
- 53 Li, J.; Ma, Y.; Mu, X.; Wang, X.; Li, Y.; Ma, H.; Guo, Z. Recent advances and perspectives on coupled water electrolysis for energy-saving hydrogen production. *Advanced Science* **2025**, *12* (7), 2411964. <https://doi.org/10.1002/advs.202411964>.
- 54 Cai, M.; Zhu, Q.; Wang, X.; Shao, Z.; Yao, L.; Zeng, H.; Wu, X.; Chen, J.; Huang, K.; Feng, S. Formation and stabilization of NiOOH by introducing α-FeOOH in LDH: composite electrocatalyst for oxygen evolution and urea oxidation reactions. *Advanced Materials* **2022**, *35* (7), 2209338. <https://doi.org/10.1002/adma.202209338>.
- 55 Zhu, Y.; Chen, Y.; Feng, Y.; Meng, X.; Xia, J.; Zhang, G. Constructing Ru-O-TM bridge in NiFe-LDH enables high current hydrazine-assisted H₂ production. *Advanced Materials* **2024**, *36* (30), 2401694. <https://doi.org/10.1002/adma.202401694>.
- 56 Guan, S.; Xu, B.; Yu, X.; Ye, Y.; Liu, Y.; Guan, T.; Yang, Y.; Gao, J.; Li, K.; Wang, J. Activation of lattice oxygen in nitrogen-doped high-entropy oxide nanosheets for highly efficient oxygen evolution reaction. *ACS Catalysis* **2024**, *14* (23), 17806-17817. <https://doi.org/10.1021/acscatal.4c05997>.
- 57 Shao, J.; Fang, Y.; Wu, X.; Abdullah, M. I.; Tao, Y. Unraveling the role of NiSnPH@OOH/CC perovskite hydroxide for efficient electrocatalytic oxidation of methanol to formate. *Nano Research* **2023**, *17* (4), 2388-2399. <https://doi.org/10.1007/s12274-023-6078-z>.
- 58 Shi, J.; Ma, J.; Ma, E.; Li, J.; Hu, Y.; Fan, L.; Cai, W. Electrochemical alcohol oxidation reaction

- on precious-metal-free catalysts: mechanism, activity, and selectivity. *Carbon Neutralization* **2024**, 3 (2), 285-312. <https://doi.org/10.1002/cnl2.116>.
- 59 Saxena, A.; Kapila, S.; Medvedeva, J. E.; Nath, M. Copper cobalt selenide as a bifunctional electrocatalyst for the selective reduction of CO₂ to carbon-rich products and alcohol oxidation. *ACS Applied Materials & Interfaces* **2023**, 15 (11), 14433-14446. <https://doi.org/10.1021/acsami.3c00488>.
 - 60 Chen, S.; Yang, X.; Tong, X.; Zhang, F.; Zou, H.; Qiao, Y.; Dong, M.; Wang, J.; Fan, W. Design of 3D hollow porous heterogeneous nickel-cobalt phosphides for synergistically enhancing catalytic performance for electrooxidation of methanol. *ACS Applied Materials & Interfaces* **2020**, 12 (31), 34971-34979. <https://doi.org/10.1021/acsami.0c08912>.
 - 61 Bambagioni, V.; Bevilacqua, M.; Bianchini, C.; Filippi, J.; Lavacchi, A.; Marchionni, A.; Vizza, F.; Shen, P. K. Self-sustainable production of hydrogen, chemicals, and energy from renewable alcohols by electrocatalysis. *ChemSusChem* **2010**, 3 (7), 851-855. <https://doi.org/10.1002/cssc.201000103>.
 - 62 Quan, L.; Jiang, H.; Mei, G.; Sun, Y.; You, B. Bifunctional electrocatalysts for overall and hybrid water splitting. *Chemical Reviews* **2024**, 124 (7), 3694-3812. <https://doi.org/10.1021/acs.chemrev.3c00332>.
 - 63 Li, S.; Ma, R.; Hu, J.; Li, Z.; Liu, L.; Wang, X.; Lu, Y.; Sterbinsky, G. E.; Liu, S.; Zheng, L.; Liu, J.; Liu, D.; Wang, J. Coordination environment tuning of nickel sites by oxyanions to optimize methanol electro-oxidation activity. *Nature Communications* **2022**, 13 (1), 2916. <https://doi.org/10.1038/s41467-022-30670-4>.
 - 64 Zhu, B.; Dong, B.; Wang, F.; Yang, Q.; He, Y.; Zhang, C.; Jin, P.; Feng, L. Unraveling a bifunctional mechanism for methanol-to-formate electro-oxidation on nickel-based hydroxides. *Nature Communications* **2023**, 14, 1686. <https://doi.org/10.1038/s41467-023-37441-9>.
 - 65 McMillan, J. D. Bioethanol production: status and prospects. *Renewable Energy* **1997**, 10 (2-3), 295-302. [https://doi.org/10.1016/0960-1481\(96\)00081-x](https://doi.org/10.1016/0960-1481(96)00081-x).
 - 66 You, B.; Liu, X.; Liu, X.; Sun, Y. Efficient H₂ evolution coupled with oxidative refining of alcohols via a hierarchically porous nickel bifunctional electrocatalyst. *ACS Catalysis* **2017**, 7 (7), 4564-4570. <https://doi.org/10.1021/acscatal.7b00876>.
 - 67 Cheng, N.; Stambula, S.; Wang, D.; Banis, M. N.; Liu, J.; Riese, A.; Xiao, B.; Li, R.; Sham, T.-K.; Liu, L.-M.; Botton, G. A.; Sun, X. Platinum single-atom and cluster catalysis of the hydrogen evolution reaction. *Nature Communications* **2016**, 7 (1), 13638. <https://doi.org/10.1038/ncomms13638>.
 - 68 Shi, Y.; Ma, Z.-R.; Xiao, Y.-Y.; Yin, Y.-C.; Huang, W.-M.; Huang, Z.-C.; Zheng, Y.-Z.; Mu, F.-Y.; Huang, R.; Shi, G.-Y.; Sun, Y.-Y.; Xia, X.-H.; Chen, W. Electronic metal-support interaction modulates single-atom platinum catalysis for hydrogen evolution reaction. *Nature Communications* **2021**, 12 (1), 3021. <https://doi.org/10.1038/s41467-021-23306-6>.
 - 69 Fu, L.; Kang, Y.; Nam, H. N.; Wang, K.; Zhou, Z.; Zhao, Y.; Phung, Q. M.; Wu, K.; Asakura, Y.; Zhou, J.; Yamauchi, Y. Harnessing work function modulation for hydrogen evolution catalysis in mesoporous bimetallic Pt-M alloys: The role of mesopores in work function optimization. *Advanced Science* **2025**, e05464. <https://doi.org/10.1002/advs.202505464>.
 - 70 Lu, Y.; Huang, K.; Cao, X.; Zhang, L.; Wang, T.; Peng, D.; Zhang, B.; Liu, Z.; Wu, J.; Zhang, Y.; Chen, C.; Huang, Y. Atomically dispersed intrinsic hollow sites of M-M₁-M (M₁ = Pt, Ir; M = Fe, Co, Ni, Cu, Pt, Ir) on FeCoNiCuPtIr nanocrystals enabling rapid water redox. *Advanced Functional Materials* **2022**, 32 (19), 2110645. <https://doi.org/10.1002/adfm.202110645>.
 - 71 Yang, F.; Huang, X.; Su, C.; Song, E.; Liu, B.; Xiao, B. 2D transition metal chalcogenides (TMDs) for electrocatalytic hydrogen evolution reaction: a review. *ChemPhysChem* **2024**, 25 (23), e202400640. <https://doi.org/10.1002/cphc.202400640>.

- 72 Liu, S.; Ye, Y.; Gao, L.; Yan, Z.; Pan, H.; Wang, Z.; Zhang, G.; Huang, X. Enhanced electrocatalytic hydrogen evolution reaction, oxygen evolution reaction and biomass oxidation over Ce-doped NiP_x via optimization of electronic modulation. *Green Chemistry* **2025**, *27*, 7307-7318. <https://doi.org/10.1039/d5gc01605c>.
- 73 Shi, Y.; Zhang, B. Recent Advances in Transition Metal Phosphide Nanomaterials: Synthesis and Applications in Hydrogen Evolution Reaction. *Chemical Society Reviews* **2016**, *45*, 1781. <https://doi.org/10.1039/C6CS90013E>.
- 74 Kim, S. K.; Qiu, Y.; Zhang, Y.-J.; Hurt, R.; Peterson, A. Nanocomposites of transition-metal carbides on reduced graphite oxide as catalysts for the hydrogen evolution reaction. *Applied Catalysis B: Environment and Energy* **2018**, *235*, 36-44. <https://doi.org/10.1016/j.apcatb.2018.04.032>.
- 75 Zhu, J.; Tu, Y.; Cai, L.; Ma, H.; Chai, Y.; Zhang, L.; Zhang, W. Defect-assisted anchoring of Pt single atoms on MoS_2 nanosheets produces high-performance catalyst for industrial hydrogen evolution reaction. *Small* **2021**, *18* (4), 2104824. <https://doi.org/10.1002/smll.202104824>.
- 76 Ryu, J.; Jung, N.; Jang, J. H.; Kim, H.-J.; Yoo, S. J. In situ transformation of hydrogen-evolving CoP nanoparticles: toward efficient oxygen evolution catalysts bearing dispersed morphologies with Co-oxo/hydroxo molecular units. *ACS Catalysis* **2015**, *5* (7), 4066-4074. <https://doi.org/10.1021/acscatal.5b00349>.
- 77 Grimaud, A.; May, K. J.; Carlton, C. E.; Lee, Y.-L.; Risch, M.; Hong, W. T.; Zhou, J.; Shao-Horn, Y. Double perovskites as a family of highly active catalysts for oxygen evolution in alkaline solution. *Nature Communications* **2013**, *4* (1), 2439. <https://doi.org/10.1038/ncomms3439>.
- 78 Lu, F.; Zhou, M.; Zhou, Y.; Zeng, X. First-row transition metal based catalysts for the oxygen evolution reaction under alkaline conditions: basic principles and recent advances. *Small* **2017**, *13* (45), 1701931. <https://doi.org/10.1002/smll.201701931>.
- 79 Subbaraman, R.; Tripkovic, D.; Chang, K.-C.; Strmcnik, D.; Paulikas, A. P.; Hirunsit, P.; Chan, M.; Greeley, J.; Stamenkovic, V.; Markovic, N. M. Trends in activity for the water electrolyser reactions on 3d M(Ni,Co,Fe,Mn) hydr(oxy)oxide catalysts. *Nature Materials* **2012**, *11* (6), 550-557. <https://doi.org/10.1038/nmat3313>.
- 80 Pham, T. H. M.; Shen, T.-H.; Ko, Y.; Zhong, L.; Lombardo, L.; Luo, W.; Horike, S.; Tileli, V.; Züttel, A. Elucidating the mechanism of Fe incorporation in in-situ synthesized Co-Fe oxygen-evolving nanocatalysts. *Journal of the American Chemical Society* **2023**, *145* (43), 23691-23701. <https://doi.org/10.1021/jacs.3c08099>.
- 81 Klaus, S.; Cai, Y.; Louie, M. W.; Trotochaud, L.; Bell, A. T. Effects of Fe electrolyte impurities on $\text{Ni}(\text{OH})_2/\text{NiOOH}$ structure and oxygen evolution activity. *The Journal of Physical Chemistry C* **2015**, *119* (13), 7243-7254. <https://doi.org/10.1021/acs.jpcc.5b00105>.
- 82 Friebe, D.; Louie, M. W.; Bajdich, M.; Sanwald, K. E.; Cai, Y.; Wise, A. M.; Cheng, M.-J.; Sokaras, D.; Weng, T.-C.; Alonso-Mori, R.; Davis, R. C.; Bargar, J. R.; Nørskov, J. K.; Nilsson, A.; Bell, A. T. Identification of highly active Fe sites in $(\text{Ni,Fe})\text{OOH}$ for electrocatalytic water splitting. *Journal of the American Chemical Society* **2015**, *137* (3), 1305-1313. <https://doi.org/10.1021/ja511559d>.
- 83 Zhou, D.; Xiong, X.; Cai, Z.; Han, N.; Jia, Y.; Xie, Q.; Duan, X.; Xie, T.; Zheng, X.; Sun, X.; Duan, X. Flame-engraved nickel-iron layered double hydroxide nanosheets for boosting oxygen evolution reactivity. *Small Methods* **2018**, *2* (7), 1800083. <https://doi.org/10.1002/smt.201800083>.
- 84 Pu, Z.; Liu, T.; Amiin, I. S.; Cheng, R.; Wang, P.; Zhang, C.; Ji, P.; Hu, W.; Liu, J.; Mu, S. Transition-metal phosphides: activity origin, energy-related electrocatalysis applications, and synthetic strategies. *Advanced Functional Materials* **2020**, *30* (45), 2004009. <https://doi.org/10.1002/adfm.202004009>.

- 85 Jin, S. Are metal chalcogenides, nitrides, and phosphides oxygen evolution catalysts or bifunctional catalysts? *ACS Energy Letters* **2017**, *2* (8), 1937-1938. <https://doi.org/10.1021/acsenenergylett.7b00679>.
- 86 Mishra, K.; Devi, N.; Siwal, S. S.; Thakur, V. K. Insight perspective on the synthesis and morphological role of the noble and non-noble metal-based electrocatalyst in fuel cell application. *Applied Catalysis B: Environment and Energy* **2023**, *334*, 122820. <https://doi.org/10.1016/j.apcatb.2023.122820>.
- 87 Lv, Y.; Liu, P.; Xue, R.; Guo, Q.; Ye, J.; Gao, D.; Jiang, G.; Zhao, S.; Xie, L.; Ren, Y.; Zhang, P.; Wang, Y.; Qin, Y. Cascaded p-d orbital hybridization interaction in ultrathin high-entropy alloy nanowires boosts complete non-CO pathway of methanol oxidation reaction. *Advanced Science* **2024**, *11* (19), 2309813. <https://doi.org/10.1002/adv.202309813>.
- 88 Sun, Y.; Zhou, Y.; Zhu, C.; Tu, W.; Wang, H.; Huang, H.; Liu, Y.; Shao, M.; Zhong, J.; Lee, S.-T.; Kang, Z. Synergistic Cu@CoO_x core-cage structure on carbon layers as highly active and durable electrocatalysts for methanol oxidation. *Applied Catalysis B: Environment and Energy* **2018**, *244*, 795-801. <https://doi.org/10.1016/j.apcatb.2018.12.017>.
- 89 Yang, H.; Wu, Y.; Zhuang, Z.; Li, Y.; Chen, C. Factors affecting the catalytic performance of nano - catalysts. *Chinese Journal of Chemistry* **2021**, *40* (4), 515-523. <https://doi.org/10.1002/cjoc.202100695>.
- 90 Cho, E.; Kim, S.-I.; Lee, D.-W.; You, Y.-W.; Im, M.; Kim, S. M.; Heo, I.; Choi, J.; Kim, Y. J.; Lee, J. H. Preferential chemical vapor deposition for the synthesis of the catalysts for CO mediated NO_x selective catalytic reduction. *Applied Surface Science* **2022**, *610*, 155545. <https://doi.org/10.1016/j.apsusc.2022.155545>.
- 91 Kappe, C. O. Controlled microwave heating in modern organic synthesis. *Angewandte Chemie International Edition* **2004**, *43*, 6250-6284. <https://doi.org/10.1002/anie.200400655>.
- 92 Mingos, D. M.; Baghurst, D. R. Applications of microwave dielectric heating effects to synthetic problems in chemistry. *Chemical Society Reviews* **1991**, *20*, 1-47. <https://doi.org/10.1039/CS9912000001>.
- 93 Bilecka, I.; Niederberger, M. Microwave chemistry for inorganic nanomaterials synthesis. *Nanoscale* **2010**, *2* (8), 1358. <https://doi.org/10.1039/b9nr00377k>.
- 94 Feng, S.; Xu, R. New materials in hydrothermal synthesis. *Accounts of Chemical Research* **2000**, *34* (3), 239-247. <https://doi.org/10.1021/ar0000105>.
- 95 Cundy, C. S.; Cox, P. A. The hydrothermal synthesis of zeolites: history and development from the earliest days to the present time. *Chemical Reviews* **2003**, *103* (3), 663-702. <https://doi.org/10.1021/cr020060i>.
- 96 Sekiguchi, T.; Miyashita, S.; Obara, K.; Shishido, T.; Sakagami, N. Hydrothermal growth of ZnO single crystals and their optical characterization. *Journal of Crystal Growth* **2000**, *214-215*, 72-76. [https://doi.org/10.1016/s0022-0248\(00\)00065-8](https://doi.org/10.1016/s0022-0248(00)00065-8).
- 97 Penn, R. L.; Banfield, J. F. Morphology development and crystal growth in nanocrystalline aggregates under hydrothermal conditions: insights from titania. *Geochimica Et Cosmochimica Acta* **1999**, *63* (10), 1549-1557. [https://doi.org/10.1016/s0016-7037\(99\)00037-x](https://doi.org/10.1016/s0016-7037(99)00037-x).
- 98 Taylor, C. D.; Wasileski, S. A.; Filhol, J.-S.; Neurock, M. First principles reaction modeling of the electrochemical interface: consideration and calculation of a tunable surface potential from atomic and electronic structure. *Physical Review B* **2006**, *73* (16). <https://doi.org/10.1103/physrevb.73.165402>.
- 99 Stamenkovic, V. R.; Strmcnik, D.; Lopes, P. P.; Markovic, N. M. Energy and fuels from electrochemical interfaces. *Nature Materials* **2016**, *16* (1), 57-69. <https://doi.org/10.1038/nmat4738>.

- 100 Shao, Y.; Markovic, N. M. Prelude: The renaissance of electrocatalysis. *Nano Energy* **2016**, *29*, 1-3. <https://doi.org/10.1016/j.nanoen.2016.09.025>.
- 101 Wang, Y.; Wang, D.; Li, Y. Rational design of single-atom site electrocatalysts: from theoretical understandings to practical applications. *Advanced Materials* **2021**, *33* (34), 2008151. <https://doi.org/10.1002/adma.202008151>.
- 102 Liu, L.; Corma, A. Metal catalysts for heterogeneous catalysis: from single atoms to nanoclusters and nanoparticles. *Chemical Reviews* **2018**, *118* (10), 4981-5079. <https://doi.org/10.1021/acs.chemrev.7b00776>.
- 103 Yang, X.-F.; Wang, A.; Qiao, B.; Li, J.; Liu, J.; Zhang, T. Single-atom catalysts: a new frontier in heterogeneous catalysis. *Accounts of Chemical Research* **2013**, *46* (8), 1740-1748. <https://doi.org/10.1021/ar300361m>.
- 104 Sun, Y.; Liu, T.; Li, Z.; Meng, A.; Li, G.; Wang, L.; Li, S. Morphology and interfacial charge regulation strategies constructing 3D flower-like Co@CoP₂ heterostructure electrocatalyst for efficient overall water splitting. *Chemical Engineering Journal* **2021**, *433*, 133684. <https://doi.org/10.1016/j.cej.2021.133684>.
- 105 Fan, S.; Zhang, J.; Wu, Q.; Huang, S.; Zheng, J.; Kong, D.; Chen, S.; Wang, Y.; Ang, L. K.; Shi, Y.; Yang, H. Y. Morphological and electronic dual regulation of cobalt-nickel bimetal phosphide heterostructures inducing high water-splitting performance. *The Journal of Physical Chemistry Letters* **2020**, *11* (10), 3911-3919. <https://doi.org/10.1021/acs.jpclett.0c00851>.
- 106 Feng, T.; Zeng, Q.; Lu, S.; Yang, M.; Tao, S.; Chen, Y.; Zhao, Y.; Yang, B. Morphological and interfacial engineering of cobalt-based electrocatalysts by carbon dots for enhanced water splitting. *ACS Sustainable Chemistry & Engineering* **2019**, *7* (7), 7047-7057. <https://doi.org/10.1021/acssuschemeng.8b06832>.
- 107 Ding, L.; Li, K.; Xie, Z.; Yang, G.; Yu, S.; Wang, W.; Cullen, D. A.; Yu, H.; Zhang, F. W-induced morphological modification of NiFe layered double hydroxides as efficient electrocatalysts for overall water splitting. *Electrochimica Acta* **2021**, *395*, 139199. <https://doi.org/10.1016/j.electacta.2021.139199>.
- 108 Ahsan, M. A.; He, T.; Noveron, J. C.; Reuter, K.; Puente-Santiago, A. R.; Luque, R. Low-dimensional heterostructures for advanced electrocatalysis: an experimental and computational perspective. *Chemical Society Reviews* **2022**, *51* (3), 812-828. <https://doi.org/10.1039/d1cs00498k>.
- 109 Voiry, D.; Shin, H. S.; Loh, K. P.; Chhowalla, M. Low-dimensional catalysts for hydrogen evolution and CO₂ reduction. *Nature Reviews Chemistry* **2018**, *2* (1). <https://doi.org/10.1038/s41570-017-0105>.
- 110 Saha, S.; Bansal, S.; Khanuja, M. Classification of nanomaterials and their physical and chemical nature. In *Elsevier eBooks*; 2022; pp 7-34. <https://doi.org/10.1016/b978-0-323-91009-5.00001-x>.
- 111 Pham, T. A.; Ping, Y.; Galli, G. Modelling heterogeneous interfaces for solar water splitting. *Nature Materials* **2017**, *16* (4), 401-408. <https://doi.org/10.1038/nmat4803>.
- 112 Li, Y.; Zhang, J.; Chen, Q.; Xia, X.; Chen, M. Emerging of heterostructure materials in energy storage: a review. *Advanced Materials* **2021**, *33* (27), 2100855. <https://doi.org/10.1002/adma.202100855>.
- 113 Suryanto, B. H. R.; Wang, Y.; Hocking, R. K.; Adamson, W.; Zhao, C. Overall electrochemical splitting of water at the heterogeneous interface of nickel and iron oxide. *Nature Communications* **2019**, *10*, 5599. <https://doi.org/10.1038/s41467-019-13415-8>.
- 114 Wu, T.; Guo, R.-T.; Li, C.-F.; You, Y.-H.; Pan, W.-G. Recent advances in core-shell structured catalysts for low-temperature NH₃-SCR of NO_x. *Chemosphere* **2023**, *333*, 138942.

<https://doi.org/10.1016/j.chemosphere.2023.138942>.

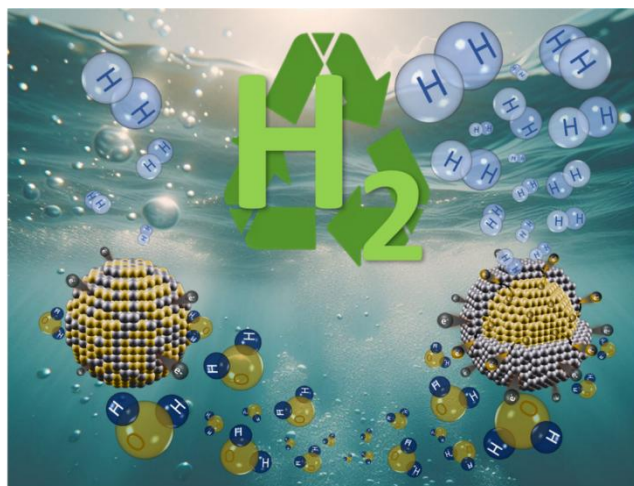
- 115 Zhang, A.; Liang, Y.; Zhang, H.; Geng, Z.; Zeng, J. Doping regulation in transition metal compounds for electrocatalysis. *Chemical Society Reviews* **2021**, *50* (17), 9817-9844. <https://doi.org/10.1039/d1cs00330e>.
- 116 Wang, Y.; Yuan, F.; Li, Z.; Zhang, D.; Yu, Q.; Wang, B. Heteroatom-doped carbon anode materials for potassium-ion batteries: from mechanism, synthesis to electrochemical performance. *APL Materials* **2022**, *10* (3), 030902. <https://doi.org/10.1063/5.0086874>.
- 117 Leube, B. T.; Robert, C.; Foix, D.; Porcheron, B.; Dedryvère, R.; Rousse, G.; Salager, E.; Cabelguen, P.-E.; Abakumov, A. M.; Vezin, H.; Doublet, M.-L.; Tarascon, J.-M. Activation of anionic redox in d0 transition metal chalcogenides by anion doping. *Nature Communications* **2021**, *12*, 5485. <https://doi.org/10.1038/s41467-021-25760-8>.
- 118 Niu, S.; Jiang, W.-J.; Wei, Z.; Tang, T.; Ma, J.; Hu, J.-S.; Wan, L.-J. Se-doping activates FeOOH for cost-effective and efficient electrochemical water oxidation. *Journal of the American Chemical Society* **2019**, *141* (17), 7005-7013. <https://doi.org/10.1021/jacs.9b01214>.
- 119 Zhang, K.; Zhang, G.; Qu, J.; Liu, H. Disordering the atomic structure of Co(II) oxide via B-doping: an efficient oxygen vacancy introduction approach for high oxygen evolution reaction electrocatalysts. *Small* **2018**, *14* (41), 1802760. <https://doi.org/10.1002/smll.201802760>.
- 120 Gao, S.; Zhao, S.; Tang, X.; Sun, L.; Li, Q.; Yi, H. Research on the application of defect engineering in the field of environmental catalysis. *Green Energy & Environment* **2024**, *10*: 1187-1209. <https://doi.org/10.1016/j.gee.2024.08.008>.
- 121 Wu, Z.; Zhao, Y.; Jin, W.; Jia, B.; Wang, J.; Ma, T. Recent progress of vacancy engineering for electrochemical energy conversion related applications. *Advanced Functional Materials* **2020**, *31* (9), 2009070. <https://doi.org/10.1002/adfm.202009070>.
- 122 Escudero-Escribano, M.; Verdaguer-Casadevall, A.; Malacrida, P.; Grønbjerg, U.; Knudsen, B. P.; Jepsen, A. K.; Rossmeisl, J.; Stephens, I. E. L.; Chorkendorff, I. Pt₅Gd as a highly active and stable catalyst for oxygen electroreduction. *Journal of the American Chemical Society* **2012**, *134* (40), 16476-16479. <https://doi.org/10.1021/ja306348d>.
- 123 Schmidt, T. J.; Gasteiger, H. A.; Stäb, G. D.; Urban, P. M.; Kolb, D. M.; Behm, R. J. Characterization of high - surface - area electrocatalysts using a rotating disk electrode configuration. *Journal of the Electrochemical Society* **1998**, *145* (7), 2354-2358. <https://doi.org/10.1149/1.1838642>.
- 124 Boudart, M. Turnover rates in heterogeneous catalysis. *Chemical Reviews* **1995**, *95* (3), 661-666. <https://doi.org/10.1021/cr00035a009>.
- 125 Zhang, X. L.; Jiang, Zh. H.; Yao, Zh. P.; Song, Y.; Wu, Zh. D. Effects of scan rate on the potentiodynamic polarization curve obtained to determine the Tafel slopes and corrosion current density. *Corrosion Science* **2008**, *51* (3), 581-587. <https://doi.org/10.1016/j.corsci.2008.12.005>.
- 126 Vivier, V.; Orazem, M. E. Impedance analysis of electrochemical systems. *Chemical Reviews* **2022**, *122* (12), 11131-11168. <https://doi.org/10.1021/acs.chemrev.1c00876>.
- 127 Hachtel, J. A.; Yu, S.; Lupini, A. R.; Pantelides, S. T.; Gich, M.; Laromaine, A.; Roig, A. Gold nanotriangles decorated with superparamagnetic iron oxide nanoparticles: a compositional and microstructural study. *Faraday Discussions* **2016**, *191*, 215-227. <https://doi.org/10.1039/c6fd00028b>.
- 128 Pascu, O.; Carenza, E.; Gich, M.; Estradé, S.; Peiró, F.; Herranz, G.; Roig, A. Surface reactivity of iron oxide nanoparticles by microwave-assisted synthesis; comparison with the thermal decomposition route. *The Journal of Physical Chemistry C* **2012**, *116* (28), 15108-15116.

<https://doi.org/10.1021/jp303204d>.

- 129 Yu, S.; Hachtel, J. A.; Chisholm, M. F.; Pantelides, S. T.; Laromaine, A.; Roig, A. Magnetic gold nanotriangles by microwave-assisted polyol synthesis. *Nanoscale* **2015**, 7 (33), 14039-14046. <https://doi.org/10.1039/c5nr03113c>.
- 130 May-Masnou, A.; Soler, L.; Torras, M.; Salles, P.; Llorca, J.; Roig, A. Fast and simple microwave synthesis of TiO₂/Au nanoparticles for gas-phase photocatalytic hydrogen generation. *Frontiers in Chemistry* **2018**, 6, 110. <https://doi.org/10.3389/fchem.2018.00110>.
- 131 Torras, M.; Molet, P.; Soler, L.; Llorca, J.; Roig, A.; Mihi, A. Au/TiO₂ 2D-photonic crystals as UV-visible photocatalysts for H₂ production. *Advanced Energy Materials* **2021**, 12 (6), 2103733. <https://doi.org/10.1002/aenm.202103733>.
- 132 Torras, M.; Roig, A. Copper oxide nanocubes wrapping metals by microwave synthesis. *Crystal Growth & Design* **2021**, 21 (9), 5027-5035. <https://doi.org/10.1021/acs.cgd.1c00462>.

Chapter 2

AuPt Nanostructures with a High Hydrogen Evolution Reaction Activity through a Halide-mediated Microwave-assisted Route



The results presented in this chapter have been published in Journal of Materials Chemistry A as “*AuPt nanostructures with a high hydrogen evolution reaction activity through a halide-mediated microwave assisted route*” by Xuesong Zhang, Jesús Chacón-Borrero, Ren He, Jaume Gázquez, Miquel Torras, Andreu Cabot, Anna Roig, and Pablo Guardia (<https://doi.org/10.1039/d4ta04545a>). The text and figures have been adapted for the purpose of this thesis: the introduction was slightly revised, and some figures were re-edited for consistency with the thesis format. No additional experimental data beyond the published work are included in this chapter.

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Chapter Summary

In light of the escalating scarcity and rising costs of platinum (Pt), it is imperative to take a strategic approach to its rational utilization as an electrocatalyst for the hydrogen evolution reaction (HER). In this chapter, we present a novel microwave (MW)-assisted synthesis route combined with the addition of halide ions, specifically chloride, for the synthesis of AuPt nanostructured electrocatalysts. By adjusting the Au:Pt ratio in solution, as well as the halide concentration, we achieve control over the composition, size, shape, and structure of the nanocrystals (NCs). Comparative analysis of the HER electrocatalytic activity revealed that samples produced in the presence of chloride exhibit reduced overpotentials and increased mass activities. Notably, when using a 1:4 Au:Pt ratio and 0.12 mmols of HCl, NCs display lower overpotential and Tafel slope values compared to commercial platinum carbon (Pt/C) catalyst ($24 \text{ mV}@10 \text{ mA}\cdot\text{cm}^{-2}$ and $13 \text{ mV}\cdot\text{dec}^{-1}$, compared to $31 \text{ mV}@10 \text{ mA}\cdot\text{cm}^{-2}$ and $30 \text{ mV}\cdot\text{dec}^{-1}$, respectively). Moreover, this nanostructure exhibits a 6.9-fold higher mass activity compared to Pt/C ($13.8 \text{ A}\cdot\text{mg}^{-1}_{\text{Pt}}$ and $2.0 \text{ A}\cdot\text{mg}^{-1}_{\text{Pt}}$, respectively). We attribute the enhancement in electrocatalytic performance to the formation of an Au-rich core supporting a Pt shell structure, which maximizes the exposure of Pt atoms. This synthesis route offers a pathway to produce Pt-based catalysts with superior electrocatalytic performance for HER, contributing to the rational use of Pt in green hydrogen production.

2.1 Introduction

Compared to synthetic carbon-based fuels, hydrogen holds the potential for achieving carbon neutrality or even a negative carbon footprint throughout its life cycle.¹ As we mentioned in **Chapter 1**, around 96% of the world's hydrogen is produced from fossil fuels, predominantly via steam methane reforming, with only 4% generated through water electrolysis.^{2,3} Splitting water employing electrical current from renewable energy sources represents zero CO₂ emission hydrogen production, commonly referred to as green hydrogen.⁴ As shown in **Section 1.2.2**, the water splitting process encompasses two half-reactions: hydrogen evolution (HER) at the cathode and oxygen evolution (OER) at the anode. To overcome the energy barrier of these electrochemical processes, voltages as high as 1.8 V may be required. In this scenario, electrocatalysts are key actors in lowering high overpotentials (η), enhancing efficiency, and reducing the total energy consumption of hydrogen production.⁵ Consequently, developing active, stable, and cost-effective electrocatalysts for water splitting is critical for a green hydrogen-based economy. As the reaction mechanisms and kinetic characteristics of the cathodic HER have been systematically discussed in **Section 1.3.1**, they will not be reiterated in this chapter.

Non-noble metal catalysts, such as metal-sulfides, -nitrides and -phosphides nanomaterials, have attracted significant attention in the past decade.^{6–8} Nevertheless, they exhibit lower stability and activity in water splitting compared to noble-metal catalysts (e.g., Pt, Ir or Ru).^{9–11} Indeed, Pt-based catalysts deliver high current densities at low overpotentials for HER,^{12–14} as depicted in [Figure 1.4](#). In that regard, despite their scarcity, the trade-off between the reduced energy consumption and the cost of Pt-based catalysts is considered advantageous. As such, the energy savings from lowering the cell operating voltage by 0.1 V can be up to ten times the cost of the Pt electrocatalyst.¹⁵

Multi-metallic nanocrystals (NCs) represent an appealing platform for developing low-Pt content catalysts providing unique physicochemical and catalytic properties resulting from the modulation of electronic states.^{16–20} For instance, bimetallic (PtRu, Pt₃Ni, PtNi, Pt₃Co or Pt₃Fe)^{21–23} or high entropy alloys (e.g., FeCoNiPtIr)^{24,25} have shown remarkable catalytic activity for low Pt loadings. In parallel, alternative strategies such as depositing a Pt atomic layer shell onto metallic cores,²⁶ single Pt atom

decoration on carbon or metal oxides matrices,^{27,28} or the atomic Pt functionalization of porous structures^{29,30} have reported noteworthy progresses in this field.

Among multi-metallic structures, Au-based alloys have garnered much attention in the last decade with a plethora of well-established synthetic approaches.^{31,32} Despite the low binding energy and high overpotential of Au atoms for the HER,³³ alloyed electrocatalysts such as AuCu, AuPd, or AuNi have attracted interest due to their excellent activity combined with durability and low precious metal content.³⁴ In the particular case of AuPt alloys, the combination of a Pt d-band shift with the proportional competencies of Au and Pt atoms has led to enhanced catalytic efficiency.³⁵ Moreover, Au stabilizes the Pt increasing the durability of AuPt catalysts by up to 30 times.³⁶

The combination of Au and Pt into a structure has been proven to provide significant advances in the activity and stability of electrocatalysts for acidic HER. On the one hand, controlling the stoichiometry in AuPt bimetallic alloys has an impact in reducing overpotentials, as reported for Au₁Pt₈ NCs with $\eta = 26$ mV at $10 \text{ mA} \cdot \text{cm}^{-2}$.³⁷ On the other hand, Au-Pt heterostructures such as Au_{38.4}@Au_{9.3}Pt_{52.3} or Au@PtIr core-shell NCs have also demonstrated outstanding activities.^{38,39} In that direction, strain engineering in Au@PtCo_{0.05} core-shell structures has been reported to modulate the Pt d-band position.⁴⁰ Nowadays, Au-Pt nanostructures are predominantly produced following two-step approaches (e.g., seed-mediated growth), thus increasing production costs while limiting mass production.³² Simultaneously, ultra-small AuPt NCs (below 3 nm) or the control over shape are highly desirable despite their compromised stability.⁴¹ MW-assisted approaches have been successfully employed to produce metal or alloyed NCs but with limited control over the formation of complex structures such as dumbbell-like or core-shell alloys.^{42,43} In that regard, halide ions have been identified as shape directors in the synthesis of metallic NCs^{44–46} or as interphase mediators in the growth of semiconductor core-shell structures.^{47–49} Noteworthy, the effect of halide ions in the synthesis of alloys has received limited attention, particularly within the context of MW-assisted synthesis approaches.

Herein, we report on the MW-assisted synthesis of AuPt bimetallic NCs showing exceptional performance as electrocatalysts for the HER under acidic conditions. These NCs were produced by exposing a solution containing Au and Pt precursors to MW radiation for 10 min. By adjusting the Au to Pt precursor molar ratio, various

shapes, including spheres, clusters, and peanut-shaped NCs were synthesized. Interestingly, the controlled addition of halide ions in the reaction solution, such as chloride, provided further control over the shapes, resulting in the formation of core-shell structures. The electrocatalytic activity for the HER in acidic media revealed a significant correlation between the Au to Pt feeding ratio or the presence of chloride. Noteworthy, despite the inherent lack of activity for HER of Au, the AuPt core-shell structures showed remarkable activities, surpassing those of commercial Pt/C. In particular, overpotentials as low as 24 mV @ 10 mA·cm⁻² along with a mass activity up to 6.9-fold higher compared to that of commercial Pt/C. On the one hand, these results emphasize the primary influence of chloride in modulating the reaction kinetics of Au and Pt, leading to the growth of an Au-rich core surrounded by a thin Pt shell. On the other hand, the presence of an Au core appears to be responsible for the enhanced catalytic activity of AuPt NCs compared to state-of-the-art Pt and Pt-based catalysts.

2.2 Experimental

This section describes the details of the chemicals used in the reaction, synthesis process, ligand removal, characterization techniques, and electrochemical measurements.

2.2.1 Materials

Tetrachloroauric(III) acid trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, $\geq 99.9\%$), chloroplatinic acid hydrate ($\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$, $\geq 99.9\%$), hydrochloric acid (HCl , 37%), polyvinylpyrrolidone ($\text{PVP}_{10\text{k}}$, $M_w = 10,000$), sodium borohydride (NaBH_4 , 99%), Nafion 117 (~5% solution in a mixture of lower aliphatic alcohols and water) and 2-propanol ($\geq 99.5\%$) were purchased from Sigma-Aldrich. Ethylene glycol (EG, $\geq 99\%$), ethanol and acetone were purchased from Panreac. Carbon black (Vulcan CX-72) was purchased from FuelCellStore. Commercial Pt/C (20 wt.% on Vulcan) was purchased from Quintech. Sulfuric acid (H_2SO_4 , 98%) was purchased from Fisher Chemical. All materials were used as received without further purification. Milli-Q water ($18.2 \text{ M}\Omega \cdot \text{cm}$, Milli-Q IQ, Merck Millipore) was employed for all experiments and solutions.

2.2.2 Synthesis of AuPt NCs

Samples were synthesized in a MW reactor (CEM Discover SP) operating at a frequency of 2.45 GHz and a power of 300 W. Solutions were placed inside the reactor and heated to the desired temperature by applying MW radiation. Temperature control was achieved by applying pulsed MW radiation. The samples produced by the MW-assisted approach were compared to those synthesized using a conventional oil-bath approach. [Figure 2.1](#) shows a simplified schematic diagram of the synthesis process.

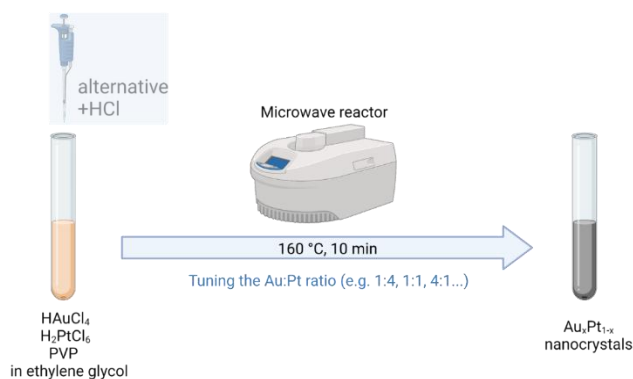


Figure 2.1 Schematic diagram of the synthesis of AuPt NCs

MW-assisted Synthesis of AuPt NCs

In a standard procedure for the synthesis of AuPt NCs, 25 mg of PVP_{10k} was placed in a 10 mL reaction tube and dissolved in 4 mL of ethylene glycol by continuous sonication (ca. 20 min). Next, 5.6 μL and 22.4 μL of 289 mM solutions of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ and $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$, respectively, were added to the reaction tube resulting in a homogeneous yellowish-colored solution. The final metal ion concentration was 2 mM (Au and Pt). Thereafter, the tube was placed in the MW reactor and heated up to 160 °C (ca. 90 seconds). After 10 min at this temperature, the reaction tube was cooled down and 30 mL of acetone was added, followed by centrifugation at 6000 rpm for 10 min. The supernatant was discarded, and the solid precipitate dispersed in 1 mL of MQ- H_2O . The NCs were further washed by adding 10 mL of acetone to the solution and centrifuging it at 6000 rpm for 10 min. This washing procedure was repeated at least twice before dispersing the final sample into 1 mL of MQ- H_2O . According to the Au to Pt molar feeding ratio, the sample was labelled as AuPt_{1/4}.

Samples with different Au:Pt molar ratios were synthesized by following the above-described procedure but varying the volumes of the Au and Pt metal stock solutions added to the reaction solution. Regardless of the Au:Pt ratio, the total volume of the metal solutions (Au and Pt) was kept constant (28 μL), resulting in a 2 mM final metal ion concentration. Samples were labelled according to the Au:Pt feeding molar ratio: Pt (0:1), AuPt_{1/6} (1:6), AuPt_{1/4} (1:4), AuPt_{1/2} (1:2), AuPt_{1/1} (1:1), AuPt_{2/1} (2:1), AuPt_{4/1} (4:1), AuPt_{6/1} (6:1), and Au (1:0).

Halide-mediated Synthesis of AuPt NCs

Following the above-described procedure, a given amount of chloride was introduced into the solution by adding a hydrochloric acid solution (HCl, 37 wt%). For instance, 10 μL (122 μmol of HCl) were added into a 4 mL of ethylene glycol solution containing 25 mg of PVP_{10k}, 5.6 μL of $\text{HAuCl}_3 \cdot 3\text{H}_2\text{O}$ solution (289 mM) and 22.4 μL of $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ solution (289 mM). The remaining procedures were identical to the ones described above, and these samples were labelled as AuPt_{1/4Cl}. Various samples (Pt_{Cl}, AuPt_{1/6Cl}, AuPt_{1/4Cl}, AuPt_{1/2Cl}, AuPt_{1/1Cl}, AuPt_{2/1Cl}, AuPt_{4/1Cl}, AuPt_{6/1Cl}, Au_{Cl}) were produced by varying the Au:Pt ratios while keeping the HCl amount constant (0:1, 1:6, 1:4, 1:2, 1:1, 2:1, 4:1, 6:1, and 1:0, respectively).

Ligand Removal

The above-produced NCs were coated by PVP_{10k} molecules, forming an organic shell that may potentially interfere with the activity of the electrocatalysts. Therefore, PVP_{10k} was removed from the surface of the AuPt NCs following a reported approach with minor modifications.⁵⁰ In a typical procedure, 10 mg of AuPt_{1/4Cl} NCs were dispersed by sonication in 20 mL of a NaBH₄/ethanol/H₂O solution (10 mg/10 mL/10 mL) for 3 min at room temperature. After sonication, 30 mL of ethanol was added to the mixture and NCs were collected by centrifugation (10000 rpm, 20 min). The precipitate was then washed three times with ethanol and collected by centrifugation (10000 rpm, 20 min) before being dried under ambient conditions and stored as a powder.

2.2.3 NCs Characterization

X-ray Diffraction (XRD)

XRD patterns were collected using a conventional Cu-K α radiation source ($\lambda = 1.5406$ Å) in a Bruker ADVANCE D8 with Bragg–Brentano geometry. Intensity was recorded in the 2θ range from 30 to 80° at a scanning step of 0.02°·s⁻¹. Samples were prepared by drop-casting and further evaporating a concentrated solution of NCs onto an amorphous silicon wafer.

Transmission Electron Microscopy (TEM) and High-Resolution Scanning Transmission Electron Microscopy (HR-STEM) Analyses

Electron micrographs were obtained in a JEOL 1210 TEM operating at 120 kV, equipped with a side-entry 60°/30° double tilt GATAN 646 specimen holder. HR-STEM, high-angle annular dark-field STEM (HAADF-STEM) images and STEM-energy dispersive X-ray spectroscopy (STEM-EDX) mappings were acquired using a FEI Titan microscope operated at 300 kV. Samples were prepared by drop-casting a diluted solution of NCs onto a carbon-coated Cu TEM grid (400 mesh).

Spectroscopy Characterization

Ultraviolet-visible (UV-Vis) spectra were collected on a JASCO V-780 UV-Vis-NIR spectrophotometer between 200 and 800 nm. Infrared (IR) analysis was carried out in a Fourier Transform Infrared Spectroscopy (FT-IR) Jasco 4700 spectrometer in

Attenuated Total Reflectance (ATR) accessory mode, covering the energy range from 300 to 7800 cm^{-1} . X-ray photoelectron spectroscopy (XPS) measurements were done in a SPECS PHOIBOS 150 hemispherical energy analyzer using Al K α X-ray radiation (1486.6 eV) for excitation.

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

For evaluating the final Au:Pt ratios of the NCs, ICP-OES was performed on an Agilent 5900. In order to prepare the ICP-OES solutions, samples were digested overnight by adding 100 μL NCs' solution into 1 mL of aqua regia, and the final solution was diluted to 10 mL by adding MQ-H $_2$ O.

2.2.4 Electrochemical Characterization

Catalyst Preparation

The NCs produced were supported on carbon black to assess their electrocatalytic activity. Specifically, 4 mg of AuPt NCs and 32 mg of carbon black (1:8 weight ratio) were mixed in ethanol through continuous sonication for 3 h to ensure a uniform dispersion of AuPt NCs on carbon black. After drying the suspension under vacuum at 60 $^{\circ}\text{C}$ for 6 h, 4 mg of the catalysts (AuPt NCs and carbon black) were mixed with 1 mL of a solution containing 220 μL of MQ-H $_2$ O, 750 μL of 2-propanol and 30 μL of Nafion. The mixture was then sonicated for 30 min until a homogenous ink was formed.

Electrocatalytic Performance

All electrochemical measurements were conducted at room temperature using a CHI760E electrochemical workstation (Shanghai Chenhua Instrument Co. Ltd., China). A standard three-electrode cell configuration with a glassy carbon (5 mm in diameter) and a graphite electrode as the working electrode (WE), a counter electrode (CE), and a Ag/AgCl electrode as the reference electrode (RE) were used. The WE was prepared by polishing the surface before drop casting 5 μL of the AuPt NCs ink (see section above). The final Au and Pt metal loadings were determined by ICP-OES for each sample (see [Table 2.1](#)). Linear sweep voltammetry (LSV) was conducted at a scan rate of 5 $\text{mV}\cdot\text{s}^{-1}$ from 0 to -0.6 V (vs. Ag/AgCl) in a 0.5 M H $_2$ SO $_4$ electrolyte. All potentials were corrected to the reversible hydrogen electrode (RHE) by following the

Nernst equation: $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.0591 \cdot \text{pH} + 0.197 \text{ V}$. All the data were corrected for the 90% iR compensation manually. The electrochemical double-layer capacitance (C_{dl}) curves of the catalysts were measured by cyclic voltammetry (CV) in the non-Faradaic region (0.397- 0.497 V vs. RHE) at scan rates from 20 to 200 $\text{mV} \cdot \text{s}^{-1}$. The C_{dl} was calculated by following the equation: $C_{\text{dl}} = \Delta j / v$, where Δj ($\Delta j = (j_{\text{a}} - j_{\text{c}}) / 2$) and v are the current density (at 0.447 V, $\text{mA} \cdot \text{cm}^{-2}$) and scan rate ($\text{mV} \cdot \text{s}^{-1}$), respectively. From the C_{dl} , the electrochemical active surface area (ECSA) was calculated as: $\text{ECSA} = C_{\text{dl}} / C_{\text{s}}$, where the general specific capacitance (C_{s}) was $0.035 \text{ mF} \cdot \text{cm}^{-2}$ in 0.5 M H_2SO_4 . Electrochemical impedance spectra (EIS) were acquired with an amplitude of 5 mV at frequencies ranging from 10^6 to 0.01 Hz. The stability of catalysts was tested by running for 4000 cycles (accelerated scan rate $200 \text{ mV} \cdot \text{s}^{-1}$) at a potential amplitude between -0.05 and -0.15 V vs. RHE. Stability over time was evaluated by voltage-time plots keeping $j = -10 \text{ mA} \cdot \text{cm}^{-2}$. Finally, the mass activity of the catalyst was calculated according to the following equations: $m_{\text{activity}} = j / m_{\text{pt}}$ or $j / m_{\text{Au+pt}}$, where j is the measured current density ($\text{mA} \cdot \text{cm}^{-2}$) and m is the loading of Pt or Au+Pt inside the catalyst (*i.e.*, $\text{Pt}/(\text{Au}+\text{Pt}) \text{ mg} \cdot \text{cm}^{-2}$).

2.3 Results and Discussion

The parameter optimization of synthesis and electrochemical measurements for HER is discussed in detail below.

2.3.1 Characterization of AuPt NCs

Size and Shape Control on AuPt NCs Absence of Chloride

According to the literature, halide atoms have been explored in the synthesis of Au and Ag NCs as shape modulators.^{51,52} In this work, we went one step further and investigated the combined effect of chloride ions and Au:Pt feeding ratios as size and shape modulators in the MW-assisted synthesis of AuPt NCs.

First, we produced NCs at different Au:Pt ratios in the absence of chloride. As is reported in [Figure 2.2](#), the size and morphology of the NCs undergo a remarkable evolution as the Au:Pt molar ratio increases. For instance, at a 0:1 molar ratio, small Pt NCs (3 ± 1 nm) can be observed, while large Au NCs (360 ± 80 nm) are produced with a 1:0 ratio, ([Figure 2.2a](#) and [i](#)). For ratios in between, the size of the NCs increases with an ascending Au:Pt ratio. This stresses the different reaction kinetics for both metals. In terms of shape evolution, the NCs evolve from pseudo-spheres ([Figure 2.2b](#) and [c](#)) or peanut-like ([Figure 2.2d](#) and [e](#)) structures at lower Au concentrations to faceted structures such as triangles ([Figure 2.2f](#)) and hexagons ([Figure 2.2g-i](#)) at higher Au content. Remarkably, samples produced with a 6:1 ratio exhibit large NCs surrounded by smaller ones, presenting a unique homogeneous morphology ([Figure 2.2h](#)). According to this observation, tuning the Au:Pt molar ratios enables the modulation of the size and shape of the NCs, likely due to the variations in the nucleation kinetics of Au and Pt. We then studied the time evolution of the NCs for a 1:1 molar ratio ([Figure 2.3](#)), observing a nucleation of small NCs already at the beginning of the reaction, which tend to aggregate after 10 min leading to worm or peanut-like shapes.

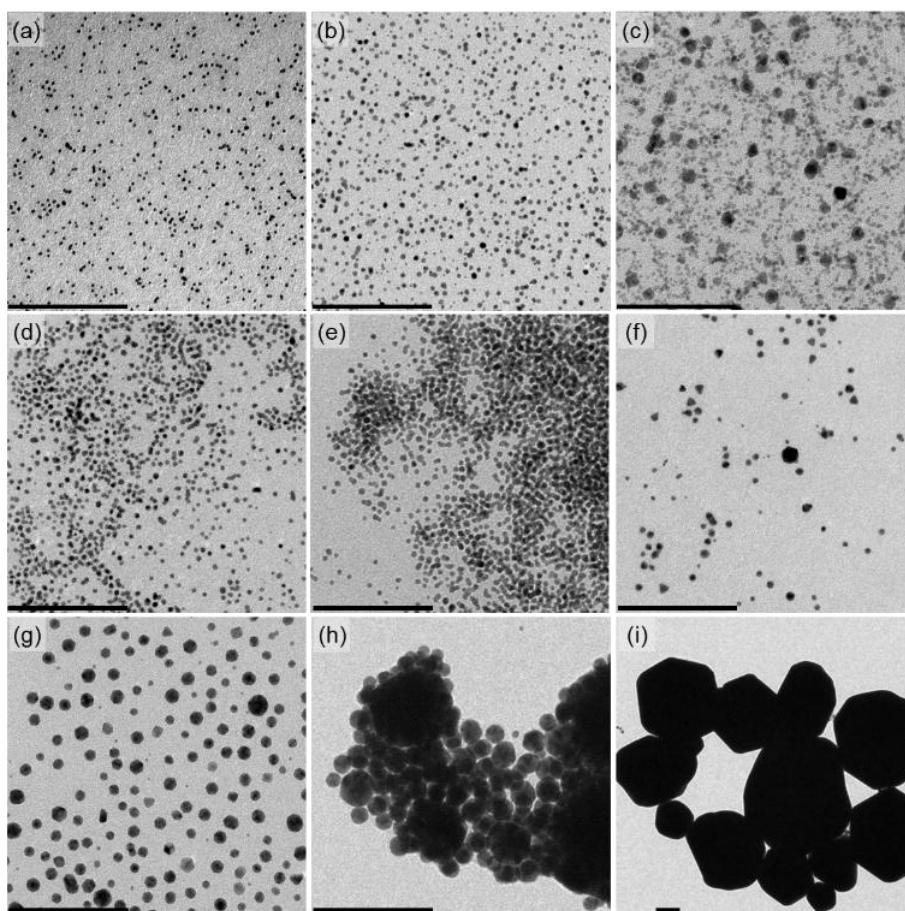


Figure 2.2 TEM images of AuPt NCs produced by a MW-assisted route at 160 °C adding different Au:Pt feeding molar ratios: (a) 0:1 - Pt, (b) 1:6 - AuPt_{1/6}, (c) 1:4 - AuPt_{1/4}, (d) 1:2 - AuPt_{1/2}, (e) 1:1 - AuPt_{1/1}, (f) 2:1 - AuPt_{2/1}, (g) 4:1 - AuPt_{4/1}, (h) 6:1 - AuPt_{6/1}, and (i) 1:0 Au. Scale bar = 100 nm

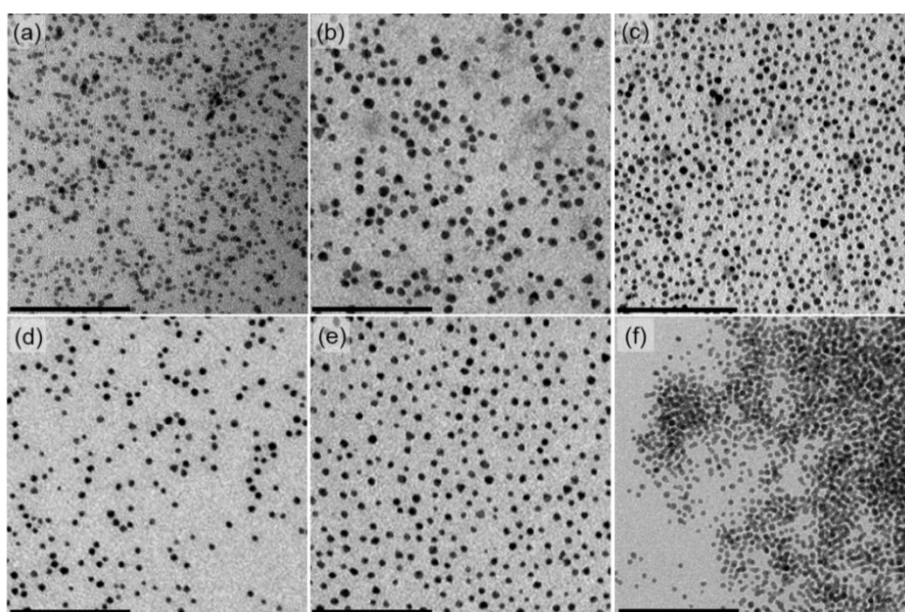


Figure 2.3 Evolution of the NCs size and morphology as a function of time for the synthesis of AuPt_{1/1}. Samples were annealed at 160 °C in a solution containing a 1:1 Au:Pt molar ratio for (a) 10 s, (b) 30 s, (c) 1 min, (d) 2 min, (e) 5 min, and (f) 10 min. Scale bar = 100 nm

To elucidate the influence of other synthetic parameters such as the amount of PVP_{10k} or the metal ion concentration, experiments increasing the amount of these reactants were carried out. On the one hand, the influence of the PVP_{10k} concentration in the reaction solution resulted in a varying trend depending on the Au:Pt ratio ([Figure 2.4](#)). For instance, at 1:0 and 0:1 ratios, the size of the NCs remains constant despite the PVP_{10k} amount. In contrast, at intermediate ratios (1:4 and 1:1), the size of the NCs increases with increasing PVP_{10k} amount, showing a stronger effect at large Au:Pt ratios. On the other hand, when the total metal molar concentration was increased from 2 mM to 8 mM while keeping the PVP_{10k} concentration constant, the size of the NCs increased ([Figure 2.5](#)). For instance, for a 1:4 Au:Pt ratio, the size of the NCs evolves from a bimodal (5 ± 1 and 9 ± 1 nm NCs at 2 mM) to a monomodal distribution (6 ± 1 at 4mM or 10 ± 2 nm at 8 mM) when the metal concentration (Au + Pt) was increased from 2 up to 8 mM, respectively ([Figure 2.5a](#) and [c](#)). When the Au:Pt ratio was increased to 1:1, the NCs size evolution followed a similar trend ([Figure 2.5d-f](#)). According to the above discussion, when the Au:Pt molar ratio is tuned, the size can be effectively modulated from small (3 ± 1 nm at a 0:1 ratio) to rather large (360 ± 80 nm at a 1:0 ratio) NCs. Conversely, the total metal molar concentration or the feeding amount of PVP_{10k} seems to have a less effect on the size and shape evolution.

Further characterization of the samples was carried out to elucidate the structure and composition of the AuPt NCs. For instance, XRD spectra revealed a shift in the [111] peak as the Au:Pt ratio increases ([Figure 2.6a](#)), which agrees with the increasing content of Au in a Pt structure. UV-vis spectra also demonstrated an evolution of the absorption with the increasing molar amount of Au. The deviation of the local surface plasmon resonance (LSPR) from its reported value for Au NCs (530 nm) is attributed to a size and composition evolution of the samples ([Figure 2.6b](#)).⁵³ For 2:1 and 4:1 ratio, this peak was located slightly below 530 nm which is consistent with the presence of Pt atoms inside a Au NCs.⁵⁴ For higher Au concentrations (*i.e.*, 6:1 and 1:0), the red-shift of the LSPR was attributed to the presence of larger NCs.⁵⁵

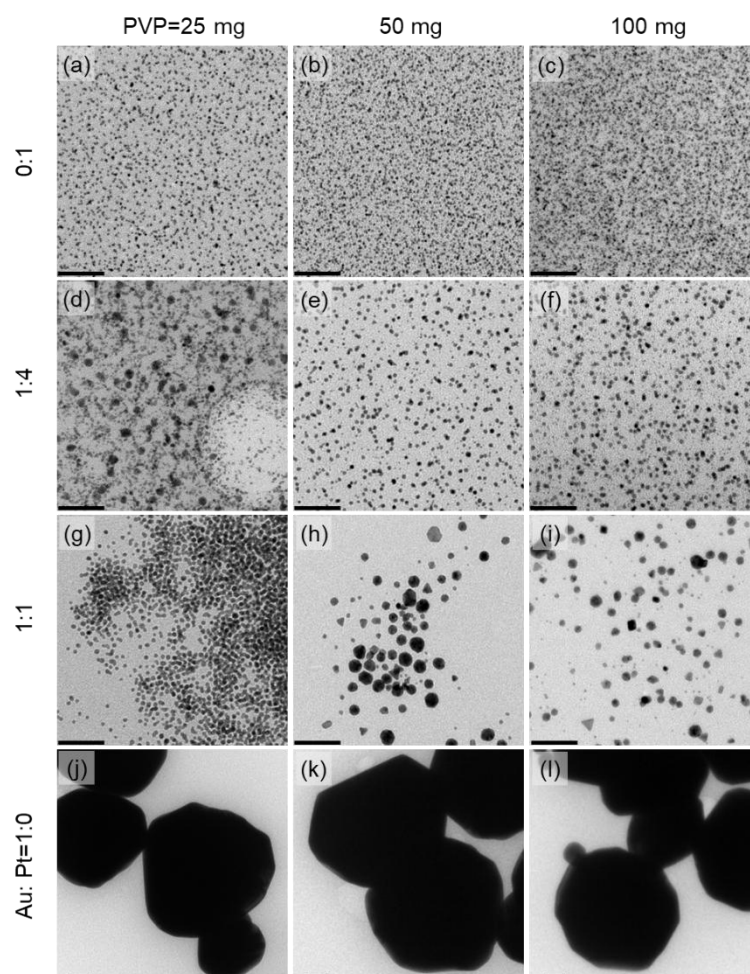


Figure 2.4 Evolution of the AuPt NCs size and shape as a function of the amount of PVP_{10K} (25, 50 and 100 mg) for different Au:Pt ratios (0:1 a-c; 1:4 d-f; 1:1 g-i; 1:0 j-k). Scale bar = 100 nm.

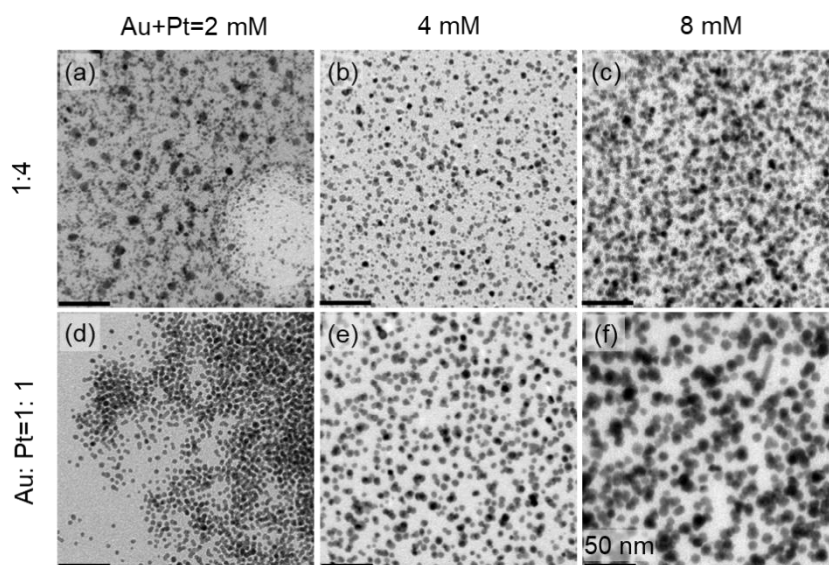


Figure 2.5 Evolution of the size and shape for AuPt NCs as a function of the total metal concentration (Au + Pt).

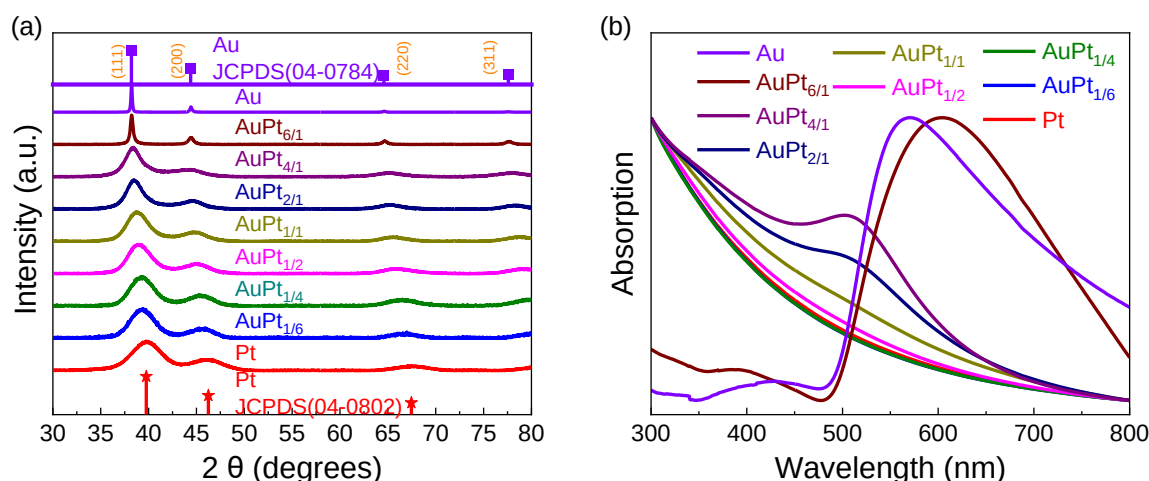


Figure 2.6 XRD and UV-Vis patterns for AuPt NCs synthesized at different Au:Pt ratios without HCl.

Size and Shape Control on AuPt NCs in the Presence of Chloride

After this initial analysis, AuPt NCs were produced following the same procedure as the previously presented samples but with the addition of a controlled amount of chloride in the solution ([Figure 2.7](#)). Despite this new set of NCs showing an increase in size with an increasing amount of Au too, the evolution of size and shape was remarkably different. For instance, from 0:1 to 1:2 ratios (Pt_{Cl} to $\text{AuPt}_{1/2\text{Cl}}$, [Figure 2.7.a-d](#)), shapes evolve from elongated or pod-like structures to nanoclusters with sizes ranging from 5 ± 1 to 14 ± 2 nm. These sizes are larger than those observed for NCs produced with the same Au: Pt ratio but without chloride ([Figure 2.2.a-d](#)). Noteworthy, we observed that samples synthesized in the presence of chloride resemble those produced without chloride but at higher Au:Pt ratios. For example, the samples produced at 1:2, 1:1, and 2:1 Au:Pt ratios in the presence of chloride ([Figure 2.7.d, e, and f](#), respectively) resemble those produced at 2:1, 4:1, and 6:1 without chloride ([Figure 2.2.f, g and h](#), respectively). This observation suggests a modulation of the nucleation kinetics mediated by chloride, likely due to the different interactions or coordination of chloride with Au and Pt ions. This point will be discussed further below.

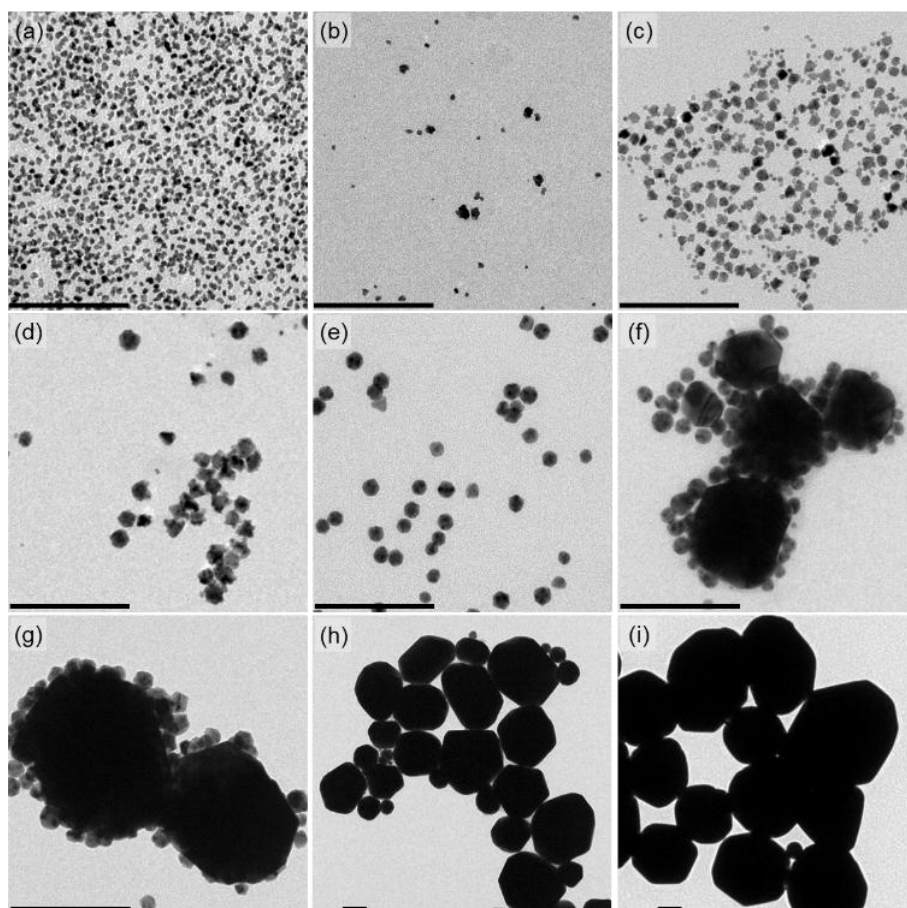


Figure 2.7 TEM images showing the evolution of the size and shape of AuPt NCs produced by adding a controlled amount of chloride with different Au:Pt ratios: (a) 0:1 - PtCl , (b) 1:6 - $\text{AuPt}_{1/6}\text{Cl}$, (c) 1:4 - $\text{AuPt}_{1/4}\text{Cl}$, (d) 1:2 - $\text{AuPt}_{1/2}\text{Cl}$, (e) 1:1 - $\text{AuPt}_{1/1}\text{Cl}$, (f) 2:1 - $\text{AuPt}_{2/1}\text{Cl}$, (g) 4:1 - $\text{AuPt}_{4/1}\text{Cl}$, (h) 6:1 - $\text{AuPt}_{6/1}\text{Cl}$, and (i) 1:0 - AuCl . Scale bar=100 nm.

The final concentration of Au and Pt within the NCs was studied through ICP-OES analysis ([Table 2.1](#) and [Figure 2.8](#)). For small Au:Pt feeding ratios, the stoichiometry of the NCs agrees with the initial metal feeding ratios for samples produced without the addition of chloride. Increasing the Au:Pt ratio up to 1:1 shows a deviation of the stoichiometry of the NCs compared to the feeding ratio but remains within reasonable agreement. However, for ratios above 1:1, the amount of Pt is smaller than the initial metal feeding. For instance, at 2:1 and 6:1 Au:Pt feeding ratios, the NCs stoichiometry is 1:0.4 and 1:0.01, respectively. In the presence of chloride, this deviation trend between NC's stoichiometry and the feeding ratio appears to be clearly enhanced, particularly above the 1:1 ratio. Indeed, for 4:1 or 6:1, the values for Pt content are below the ICP-OES detection limit, thus indicating a decrease or delay in the Pt nucleation. From these data, we concluded that a high amount of Au strongly modulates Pt nucleation and growth kinetics, inhibiting its nucleation at large

concentrations of Au (or low concentrations of Pt). This effect is enhanced when chloride was added to the reaction solution as the Au:Pt ratios of 2:1, 4:1, and 6:1 show a one-order-of-magnitude difference between samples produced with or without chloride. This led us to hypothesize the initial formation of chloride-stabilized metal clusters that modulate the reaction kinetics. To be specific, promoting the formation of more stable Pt clusters as compared to Au ones. This would delay nucleation, favoring the reduction of Pt on top of an already-formed Au core when chloride is present in the solution. Finally, the XRD peak positions evolve with increasing content of Au precursor ([Figure 2.9c](#)). The [111] peak position of the Pt structure (Pt_{Cl} sample) shifts to lower angles for sample AuPt_{1/6Cl} to AuPt_{1/1Cl}, thus indicating the possible formation of an AuPt alloy. Noteworthy, for higher Au content (AuPt_{2/1Cl}), the XRD peaks fit to an Au structure indicating the formation of an Au core. A similar trend was observed for the evolution of the LSPR ([Figure 2.9d](#)).

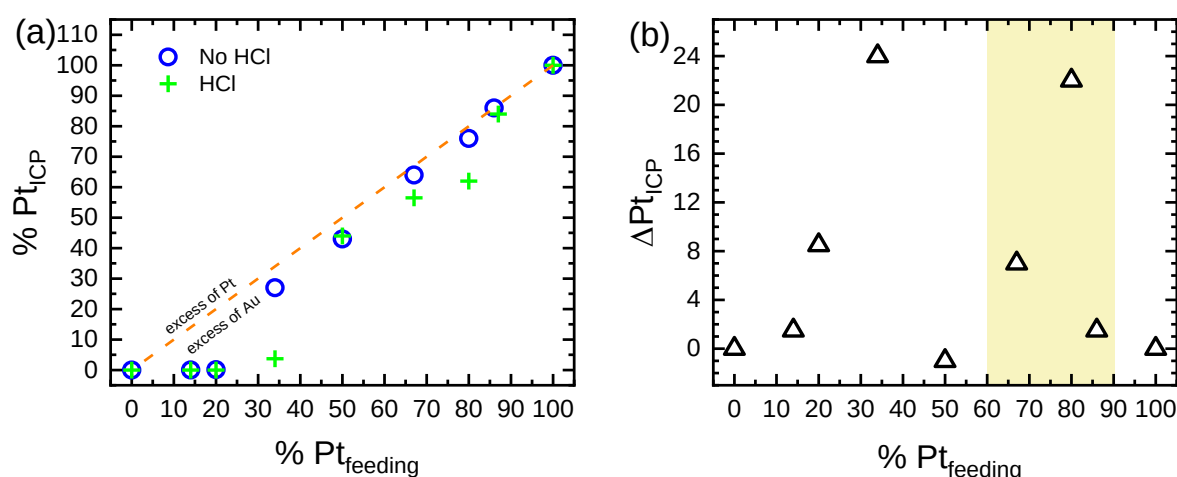
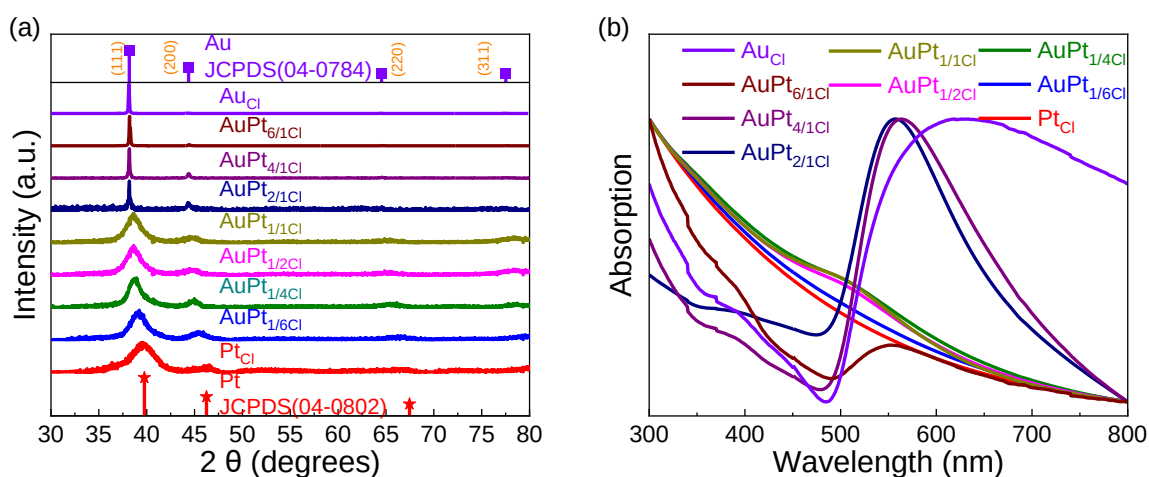


Figure 2.8 (a) Comparison between the final Pt amount inside the NCs evaluated by ICP-OES (Pt_{ICP} in %) and the Pt amount added in solution (Pt_{feeding} in %) for samples prepared under standard conditions (open blue circles) and in the presence of an excess of chlorine ions (green crosses). (b) Evaluation of the difference in Pt content (ΔPt) between samples prepared with and without excess chlorine ions as a function of Pt content in the reaction solution (Pt_{feeding} in %). The yellow area corresponds to the Pt % for the 1:6 to 1:2 Au:Pt ratio range.

Table 2.1 Summary of the structural composition for all the samples.

Samples	Au:Pt feeding ratio	Au:Pt ICP-OES ratio
Pt/C		
Pt	0:1	0:1
Pt _{Cl}		
AuPt _{1/6}	1:6	1:6.3
AuPt _{1/6Cl}		1:5.5
AuPt _{1/4}	1:4	1:3.2
AuPt _{1/4Cl}		1:1.6
AuPt _{1/2}	1:2	1:1.8
AuPt _{1/2Cl}		1:1.3
AuPt _{1/1}	1:1	1:0.7
AuPt _{1/1Cl}		1:0.8
AuPt _{2/1}	2:1	1:0.4
AuPt _{2/1Cl}		1:0.04
AuPt _{4/1}	4:1	1:0.1
AuPt _{4/1Cl}		1:0*
AuPt _{6/1}	6:1	1:0.01
AuPt _{6/1Cl}		1:0*
Au		
Au _{Cl}	1:0	1:0

* No Pt detection signal due to the limit of detection of ICP-OES equipment

**Figure 2.9** XRD and UV-Vis patterns for AuPt NCs synthesized at different Au:Pt ratios with HCl.

To investigate further the modulation by chloride in the nucleation-growth process, several volumes of a HCl solution (0, 10, 20, and 50 μL) were introduced into a reaction solution containing different Au:Pt ratios (0:1, 1:4, 1:1, and 1:0, [Figure 2.10](#)). As a general trend, we observed that increasing chloride ions leads to an increase in the

NCs size, which is consistent with a delayed or inhibited nucleation mediated by chloride-stabilized metal clusters ([Figure 2.10a-l](#)). However, when only Au was present in the solution, the size of the NCs decreased with increasing chloride concentration ([Figure 2.10m-q](#)). This highlights the opposite effect of chloride on both metal atoms: Au and Pt. In that context, adding chloride ions in the reaction solution likely promotes the formation of Au intermediates that favor nucleation against growth, thus leading to a controlled formation of NCs.⁵⁶ As for Pt, controlled conditions are likely already achieved without the addition of chloride. Consequently, an excess of chloride induces a delayed nucleation for Pt contributing to the formation of larger NCs or the reduction of Pt on top of the Au metal core. Overall, the differences in the final composition of NCs reported in [Table 2.1](#) for samples produced under the same conditions but with varying chloride ion concentrations align with the above discussion. It is worth mentioning that the stabilization of metal clusters or complexes mediated by chloride is compatible with the reported etching effect of halides in metal NCs, particularly for Ag nanocubes.⁴⁹ This suggests the nucleation and dissolution of Pt atoms during the reaction, particularly on top of Au cores, which would explain the absence of Pt under certain conditions tested in this work.

We also conducted experiments to explore the influence of different amounts of PVP_{10k} and increasing metal concentration at a fixed chloride concentration ([Figure 2.11](#) and [2.12](#)). Similar to the samples synthesized in the absence of chloride ions, excess of PVP_{10k} has a strong influence in size and shape at higher Au concentrations (e.g., 1:1 and 1:0). In this regard, increasing amounts of PVP_{10k} showed a stronger effect in the nucleation kinetics in the presence of chloride ions. In particular, a bimodal size distribution or bigger Au NCs were obtained at a 1:1 or 1:0 ratios, respectively ([Figure 2.11.g-l](#)). This observation could be attributed to a potential interplay or competition between PVP_{10k} and chloride ions, further modifying the reaction kinetics.

The effect of increasing metal concentration is enhanced in the presence of additional chloride ions ([Figure 2.12](#)). In detail, an increasing concentration of metal ions in solution (from 2 mM to 4 or 8 mM) leads to a defocusing of the size distribution, observing a bimodal distribution where small NCs surround larger ones. This observation corroborates the strong correlation between the amount of chloride and the different nucleation kinetics for each metal.

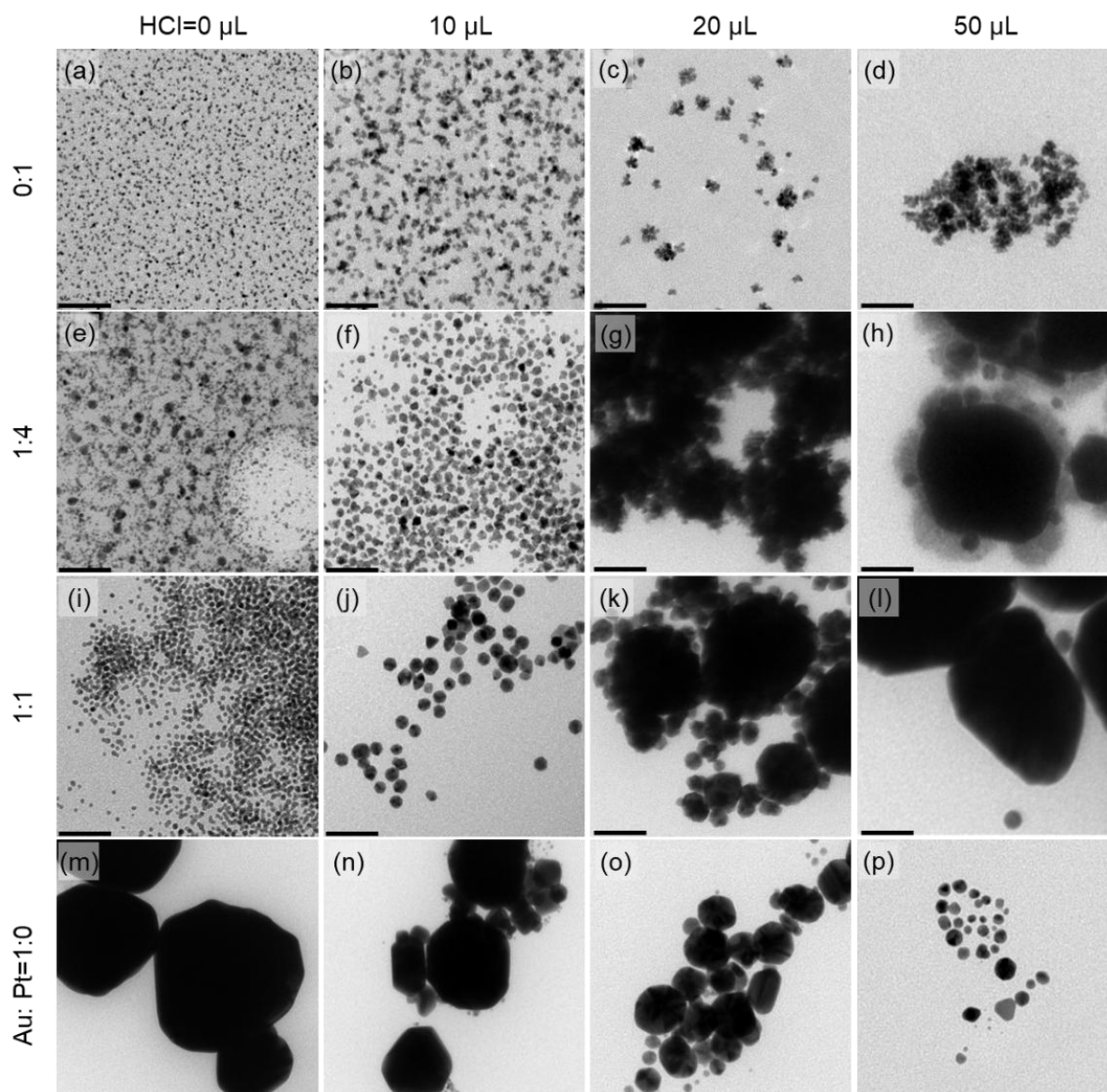


Figure 2.10 Size and shape evolution of AuPt NCs produced at different Au:Pt ratios (0:1 a-d; 1:4 e-h; 1:1 i-l; and 1:0: m-p) under different amounts of chlorine ions (0, 10, 20 and 50 μL of a 37 wt% HCl solution). Scale bar = 50 nm.

Finally, we sought to validate the influence of MW radiation on the experimental outcomes by comparing our samples with those produced under the same synthesis conditions but using conventional oil bath heating ([Figure 2.13](#)). For the 1:1 Au:Pt ratio, samples prepared both without and with the addition of chloride revealed significant disparities between both heating approaches. In particular, conventional oil bath heating resulted in larger NCs prone to nucleate in a bimodal size distribution.

Finally, the benefits of the MW-assisted approach were confirmed by a high reproducibility and potential scalability ([Figure 2.14](#)).

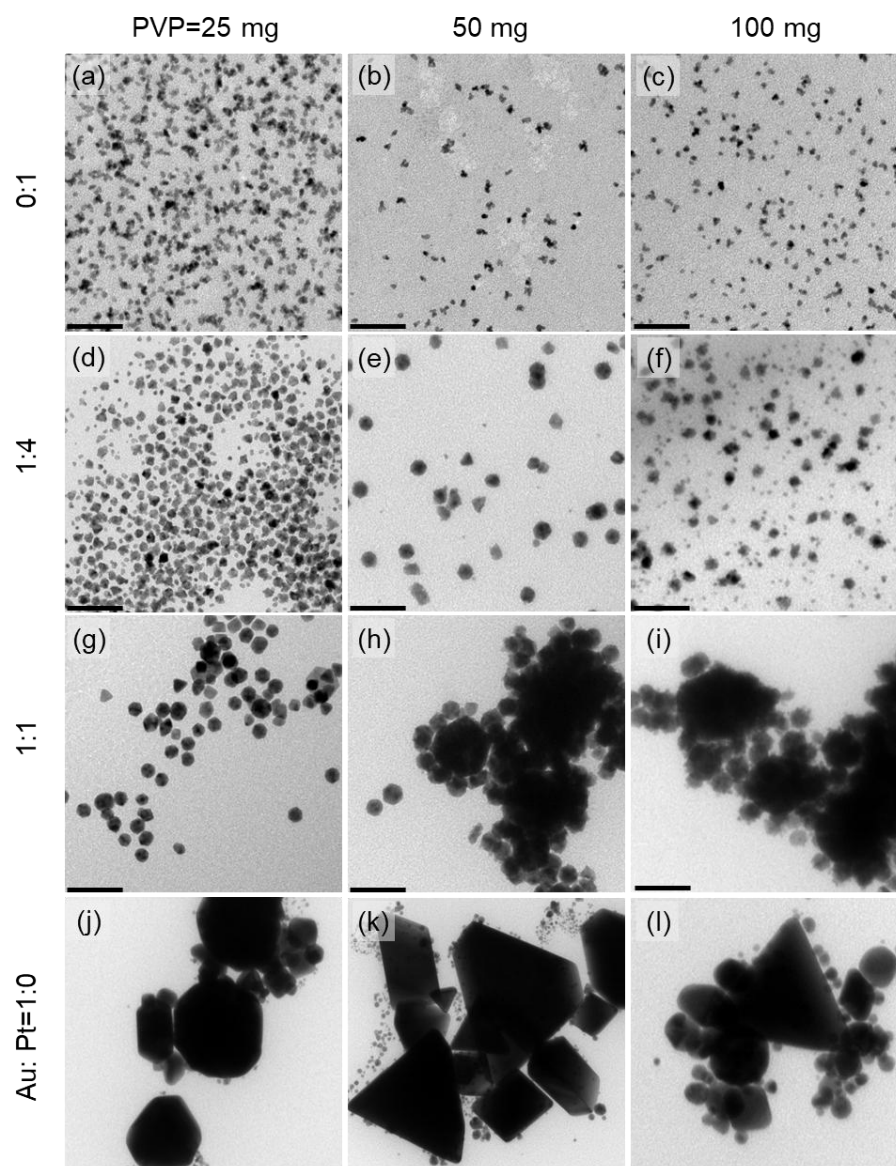


Figure 2.11 Size and shape evolution as a function of PVP_{10k} amount (25, 50 and 100 mg) for AuPt NCs produced in the presence of 10 μ L of chlorine ions. Scale bar = 50 nm.

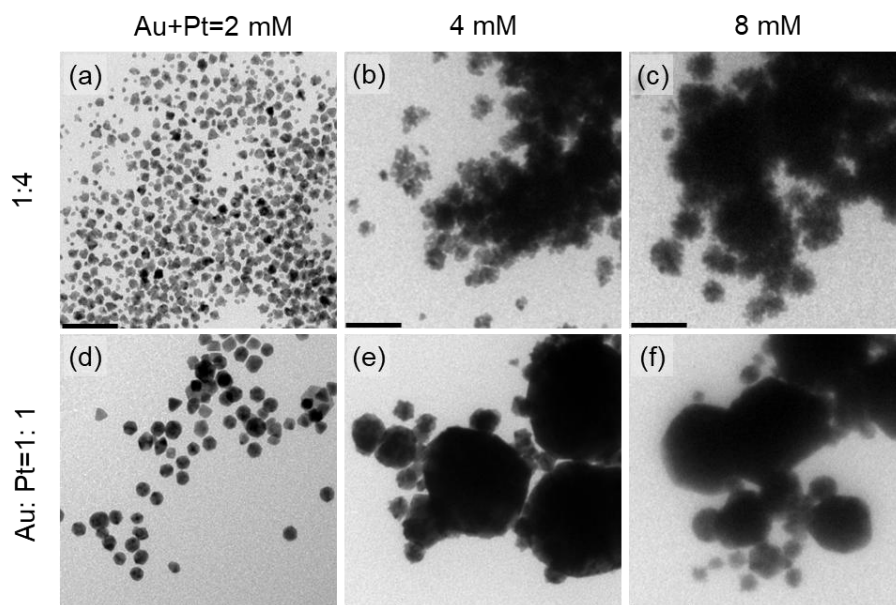


Figure 2.12 TEM images for AuPt NCs synthesized at 1:4 (a-c) and 1:1 (d-f) ratios but increasing total metal concentration (2, 4 and 8 mM). In the reaction solution, 10 μ L of HCl solution (37 wt%) were added deliberately to increase the amount of chloride ions. Scale bar = 50 nm.

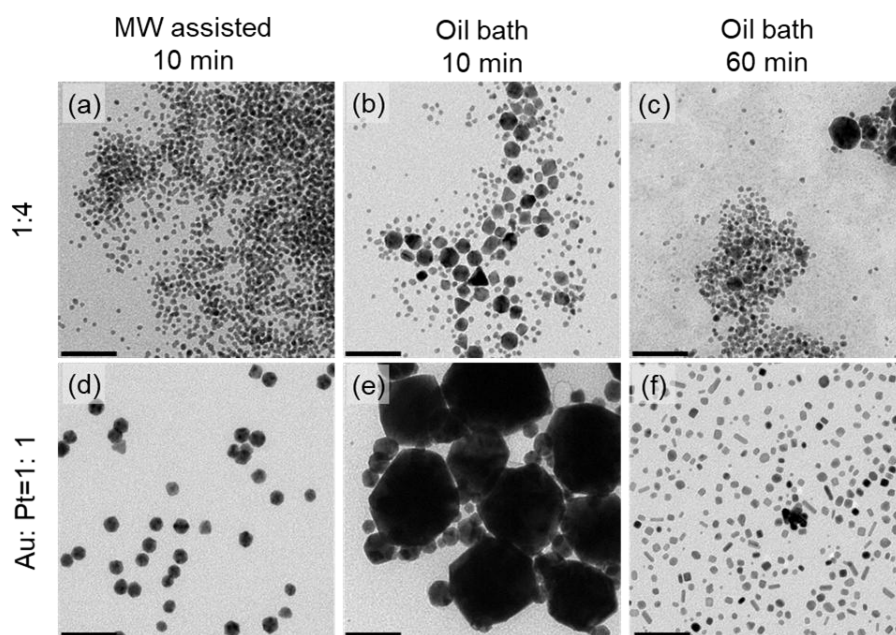


Figure 2.13 Direct comparison of AuPt NCs produced with a 1:1 Au:Pt molar ratio without or with HCl using a MW-assisted approach for 10 min (a, d) or an oil bath for 10 min (b, e) and 60 min (c, f). Scale bar = 50 nm.

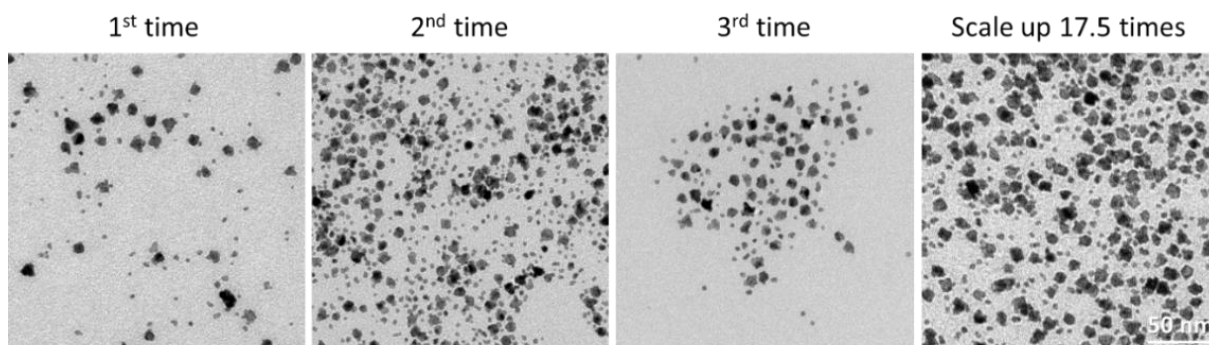


Figure 2.14 (a-c) TEM images of the NCs produced in three different experiments but under the same reaction conditions ($\text{AuPt}_{1/4\text{Cl}}$). (d) TEM image of NCs produced after scaling up the reaction condition from 4 to 70 mL (17.5-fold). The final volume was the maximum possible achieved using the flexiWAVE reactor (MilestoneTM Srl). Scale bar = 50 nm.

2.3.2 Evaluation of AuPt NCs for Hydrogen Evolution Reaction (HER)

The electrocatalytic performance of the samples was tested by LSV measurements in an Ar-saturated aqueous solution (0.5 M H_2SO_4). Before running the LSV curves, the $\text{PVP}_{10\text{k}}$ coating was removed to achieve the maximum availability of active sites on the surface.⁵⁷ $\text{PVP}_{10\text{k}}$ removal was monitored by FT-IR measurements, confirming the absence of the three characteristic peaks for $\text{PVP}_{10\text{k}}$ (1283 cm^{-1} for C-N stretching; 1422 cm^{-1} for C-H bending and 1656 cm^{-1} for C=O stretching, [Figure 2.15](#)).

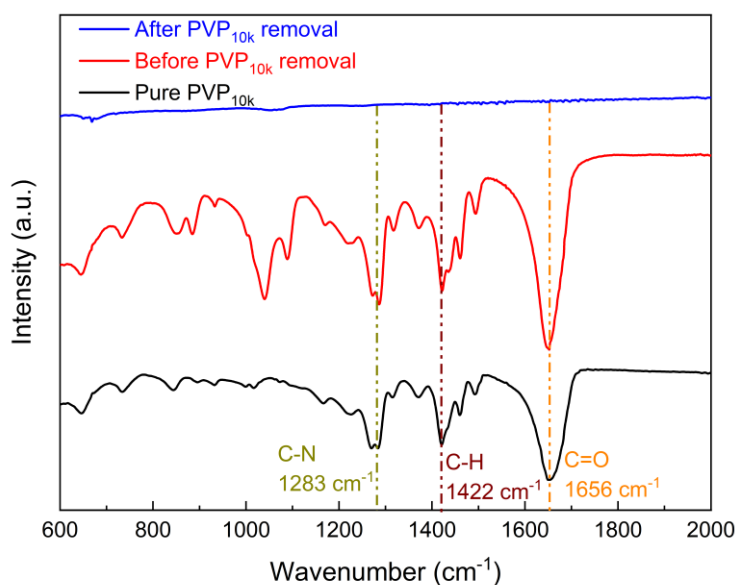


Figure 2.15 FT-IR pattern of pure $\text{PVP}_{10\text{k}}$, $\text{AuPt}_{1/1}$ before and after $\text{PVP}_{10\text{k}}$ removal.

As depicted in [Figure 2.16](#) and [Table 2.2](#), samples synthesized under standard conditions generally show increasing overpotentials as the amount of Au increases in the NCs ([Figure 2.16a](#) and [b](#)). Indeed, samples with the highest Au content (Au_{6/1} and Au_{1/0}) likely suffer from a higher hydrogen-adsorption-free energy associated with Au, resulting in poor activities.⁵⁸ When the amount of Pt increases inside the NCs, the overpotentials are similar to those for commercial Pt/C catalyst (31 mV at 10 mA·cm⁻²). For instance, samples produced with ratios ranging from 0:1 to 1:1 show overpotentials between 28 and 32 mV at 10 mA·cm⁻². Nevertheless, at higher current densities up to 100 mA·cm⁻², some of the AuPt samples exhibit lower or higher values (66 or 102 mV) than commercial Pt/C (72 mV). A similar trend is observed when analyzing the slope of the Tafel plots ([Figure 2.16c](#) and [Table 2.2](#)). In particular, AuPt_{1/2}, AuPt_{1/4}, and AuPt_{1/6} samples display slopes of 17, 26, and 23 mV·dec⁻¹, respectively, notably below that of commercial Pt/C (30 mV·dec⁻¹). Overall, when no additional chloride is added to the reaction solution, the highest performance is achieved for the AuPt_{1/2} sample, which owns a 1:1.8 Au:Pt ratio according to ICP-OES measurements ([Table 2.1](#)). Noteworthy, this result demonstrates that the activity is not directly related to the amount of Pt content.

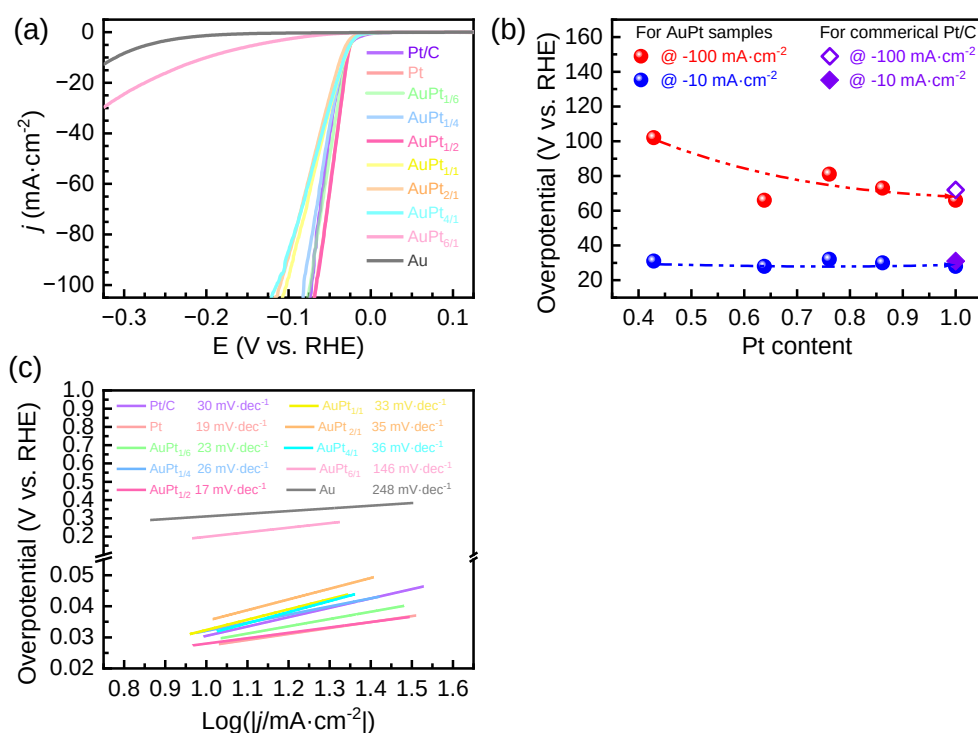


Figure 2.16 Electrocatalytic HER performance in 0.5 M H₂SO₄. (a) LSV, (b) Overpotentials vs. Pt content, and (c) Tafel slope of the AuPt NCs synthesized in the absence of chloride, respectively.

Table 2.2 Summary of the electrocatalytic performance at overpotentials @ 10 and 100 mA·cm⁻², with Tafel slopes @10 mA·cm⁻², for all the samples.

Samples	Overpotential at 10 mA·cm ⁻² (mV)	Overpotential at 100 mA·cm ⁻² (mV)	Tafel slope (mV·dec ⁻¹)
Pt/C	31	72	30
Pt	28	66	19
Pt _{Cl}	29	101	33
AuPt _{1/6}	30	73	23
AuPt _{1/6Cl}	28	58	16
AuPt _{1/4}	32	81	26
AuPt _{1/4Cl}	24	51	13
AuPt _{1/2}	28	66	17
AuPt _{1/2Cl}	28	61	17
AuPt _{1/1}	31	102	33
AuPt _{1/1Cl}	39	126	47
AuPt _{2/1}	36	110	35
AuPt _{2/1Cl}	272	#	248
AuPt _{4/1}	32	114	36
AuPt _{4/1Cl}	143	#	191
AuPt _{6/1}	200	#	146
AuPt _{6/1Cl}	360	#	266
Au	311	#	248
Au _{Cl}	390	#	134

No data collected from LSV curves

The same electrochemical characterization was carried out for the set of samples produced in the presence of an excess of chloride ions ([Figure 2.17a-c](#)). In this case, the evolution of the overpotentials as a function of the Pt content in the NCs shows a parabolic behavior, particularly for overpotentials measured at 100 mA·cm⁻². Furthermore, within the composition range of 1:6 to 1:2 Au:Pt ratio, the electrocatalytic activity is enhanced compared to samples produced under standard conditions, without the addition of chlorine. In that range, a clear minimum is observed for the AuPt_{1/4Cl} sample, which has a final Pt content of ca. 62% (1:1.63 Au:Pt ratio) and shows overpotentials of 24 and 51 mV at 10 and 100 mA·cm⁻², respectively. It is worth mentioning that these values are below those measured for commercial Pt/C catalysts (31 and 72 mV at 10 and 100 mA·cm⁻², respectively). Worth mentioning, the overpotentials are similar or even slightly higher when chloride is added for the rest of the samples. As discussed previously, the addition of chloride not only modifies the final Au:Pt content, but also promotes the formation of larger NCs. According to the general theory, larger NCs should lead to a lower activity due to the loss of active sites on the surface, as reflected in Pt and Pt_{Cl} samples (66 and 101 mV at 100 mA·cm⁻²,

respectively). Nevertheless, when comparing samples produced with or without chloride in the range from 1:6 to 1:2 Au:Pt ratio, lower overpotentials are observed when chloride is added despite the larger NCs. The same effect is observed for the Tafel slopes, observing lower slopes in the same range (*i.e.*, 1:6 to 1:2 Au:Pt ratio) when NCs were produced using an excess of chloride. Even more interestingly, the AuPt_{1/4Cl} sample demonstrates the best electrocatalytic activity towards HER despite having a lower Pt content than AuPt_{1/6Cl}. Notably, the AuPt_{1/4Cl} and AuPt_{1/2} ratios are closely aligned (1:1.63 and 1:1.76, respectively). However, their respective performance disparities highlight that catalytic activity is not solely determined by Pt content.

A straightforward comparison of the reported values for the Tafel slopes and overpotentials in the literature highlights the outstanding performance observed for our AuPt_{1/4Cl} NCs ([Figure 2.17d](#) and listed in [Table 2.3](#)). Finally, the performances measured for Pt and Pt_{Cl} samples were similar to the values measured for a commercial Pt/C catalyst.

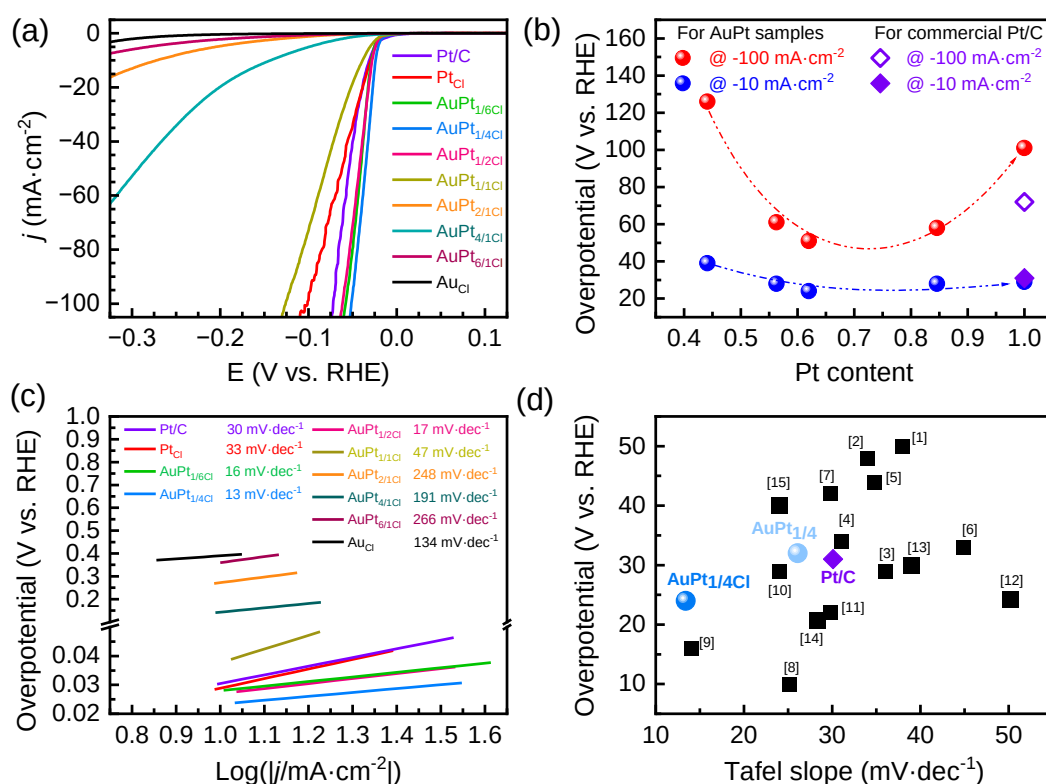


Figure 2.17 Electrocatalytic HER performance in 0.5 M H₂SO₄. (a) LSV, (b) Overpotentials vs. Pt content, and (c) Tafel slope of the AuPt NCs synthesized in the presence of chloride, respectively. (d) the comparison of as-synthesized AuPt_{1/4Cl}, AuPt_{1/4}, and Pt/C with the state-of-the-art.

Table 2.3 Summary of the specific data of the references cited in [Figure 2.17d](#)

Sample	Tafel slope (mV·dec ⁻¹)	Overpotential @ 10 mA·cm ⁻² (mV)	References
AuPt _{1/4Cl}	13	24	This work
AuPt _{1/4}	26	32	
Pt/C	30	31	
PtAu/rGO	38	50	
AuPt NDs	34	48	59
AuPtPd NDs	36	29	60
Pt _{1.88} -PVA	31	34	61
SA-Pt/MoS ₂	34.83	44	62
Pt(110)-Ni ₃ N	44.9	33	63
Pt-ACs/CoNC	29.8	42	64
PtNPs/3DHPNG/Aupla/GCE	25.2	10	65
USCS Au _{38.4} @Au _{9.3} Pt _{52.3} -NP/C	14	16	66
Pt/NBF-ReS ₂ /Mo ₂ CT _x	24	29	39
PtW ₆ O ₂₄ /C	29.8	22	67
Pt/P@Cu	50.2	24.3	68
PtHCu ₁₁ (2)	39	30	69
Pt ₅ /HMCS-5.08%	28.3	20.7	70
Pt ₁ /NMHCS	24	40	71

2.3.3 Further Characterization for AuPt_{1/4Cl}

AuPt NCs, as shown in [Figure 2.18b](#), consistent with the Au:Pt ratio measured by ICP-OES (1:3.19, as detailed in [Table 2.1](#)). In contrast, HR-HAADF images acquired from AuPt_{1/4Cl} NCs reveal a non-homogeneous contrast, particularly noticeable as blurred contrast in the core of the NC, as shown in [Figure 2.18c](#). Elemental EDX mapping further illustrates a core-shell structure wherein a Pt shell surrounds an Au core ([Figure 2.18d](#)). This observation corroborates the influence of chloride in modulating the Au and Pt nucleation/growth kinetics, favoring the nucleation of the Au core while limiting the nucleation of Pt atoms onto its surface. Some works have featured the selective binding of halide ions to different metals and the formation of various metal complexes and clusters with different reaction kinetics.⁷³ This could elucidate preferential nucleation and subsequent stabilization of Au cores over Pt ones. This hypothesis is

further supported by the observation of a lower Pt content in $\text{AuPt}_{1/4\text{Cl}}$ compared to $\text{AuPt}_{1/4}$ (1:1.63 and 1:3.19, respectively, [Table 2.1](#)). Accordingly, the higher efficiency of $\text{AuPt}_{1/4\text{Cl}}$ is unequivocally attributed to a rational distribution of the Pt atoms on the Au core's surface. This configuration not only maximizes the exposure of Pt atoms to the environment but also prevents Au atoms from interacting with the environment, thereby reducing the contribution of low-performing Au atoms to HER. Despite that, it is essential to note that this should not impede the contribution of the electron cloud of the Au core to the electrocatalytic activity, pointing towards a synergetic effect. However, this hypothesis requires further investigation beyond the scope of this work.

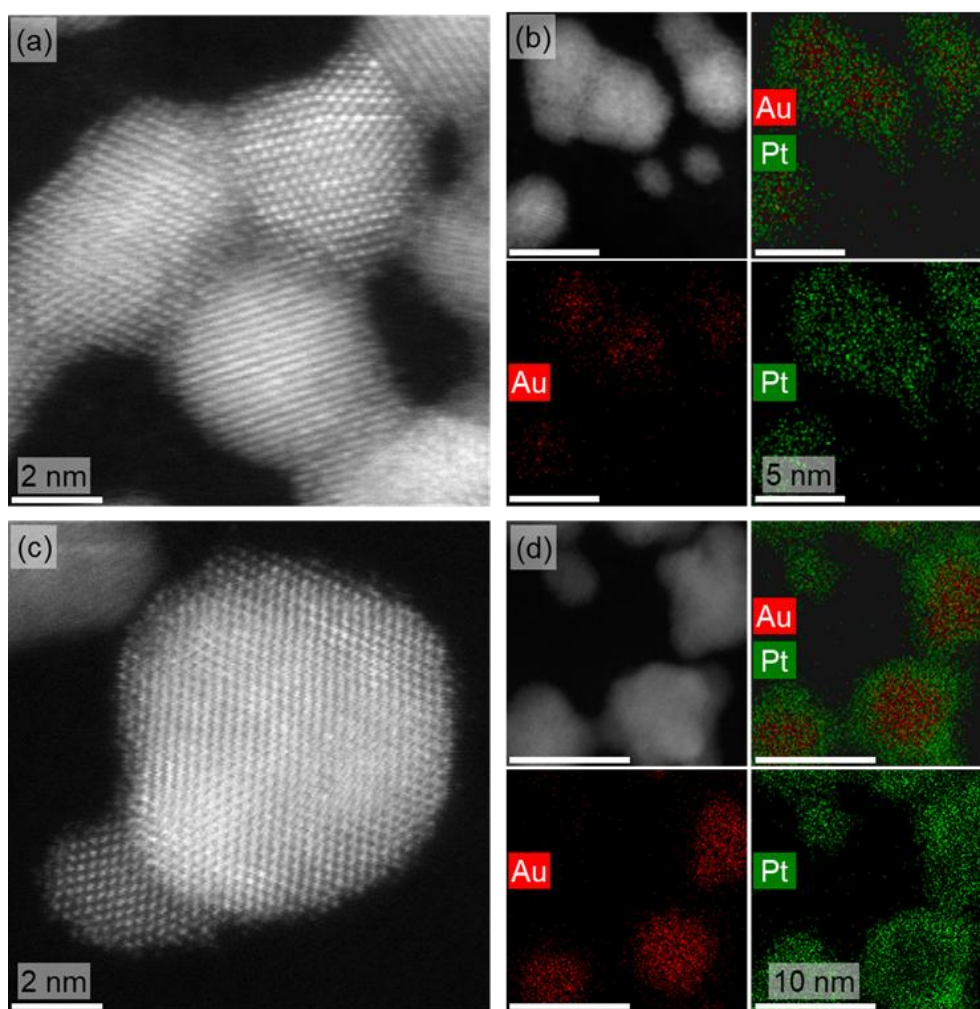


Figure 2.18 High-resolution HAADF-STEM images and EDX elemental mapping of $\text{AuPt}_{1/4}$ (a and b) and $\text{AuPt}_{1/4\text{Cl}}$ (c and d). Au and Pt elements are displayed as red and green colors, respectively.

2.3.4 Intrinsic Calculation for AuPt_{1/4Cl}

The calculation of the electrochemical active surface area (ECSA) of the three samples (Pt/C, AuPt_{1/4}, and AuPt_{1/4Cl}) by applying CV curves at different scan rates in the non-Faradaic region ([Figure 2.19a](#)) demonstrates that the core-shell heterostructure maximizes the available active Pt atoms. According to the slopes, commercial Pt/C exhibits the highest slope ($1.46 \text{ mF} \cdot \text{cm}^{-2}$), while AuPt_{1/4} and AuPt_{1/4Cl} show lower slope values (0.42 and $1.18 \text{ mF} \cdot \text{cm}^{-2}$, respectively), resulting in higher ECSA for Pt/C (41.7 cm^2) compared to AuPt_{1/4} and AuPt_{1/4Cl} (12.0 and 33.7 cm^2 , respectively). Noteworthy mentioning, the commercial Pt/C catalyst contains a 20 wt% Pt content, whereas AuPt_{1/4} and AuPt_{1/4Cl} have 8.4 and 6.9 wt% Pt content, respectively. Despite the higher number of active sites for commercial Pt/C compared to AuPt samples, its overpotential is still higher, indicating that the activity is not only related to the ECSA but also other parameters promoting the reaction. To further analyze the intrinsic activity of these electrocatalysts, their mass activities (normalized by the Pt or total metal mass) were calculated at 50 mV ([Figure 2.19b](#)). Noteworthy, the mass activity of the AuPt_{1/4Cl} is $13.8 \text{ A} \cdot \text{mg}^{-1}_{\text{Pt}}$, which is almost 6.9 times higher than that of commercial Pt/C ($2.0 \text{ A} \cdot \text{mg}^{-1}_{\text{Pt}}$) and around 3.1 times of AuPt_{1/4} ($4.4 \text{ A} \cdot \text{mg}^{-1}_{\text{Pt}}$). Therefore, arranging Pt atoms on top of a Au core likely enhances its activity while promoting interactions with the core that significantly improve the overall HER electrocatalytic performance. Certainly, when considering the total mass of the NCs (Au + Pt), these values are slightly low. For instance, $8.5 \text{ A} \cdot \text{mg}^{-1}$ for the AuPt_{1/4Cl} sample ([Figure 2.19b](#)) which represents a 4.25-fold enhancement compared to Pt/C.

To gain a better insight into the kinetic mechanism governing the HER, EIS characterization was performed on commercial Pt/C, AuPt_{1/4}, and AuPt_{1/4Cl} samples ([Figure 2.19c](#)). The estimated solution resistance (R_s) observed from the Nyquist plots is similar for all samples and in the order of 2.8 to 2.9Ω at -13 mV ([Table 2.4](#)). In this case, the semicircles can be attributed to two interfaces associated with the adsorption of species (mainly H^+ , first semicircle R_1) and the electron transfer (second semicircle R_2).⁷⁴ When comparing the R_1 values for the three samples, the AuPt_{1/4Cl} shows the lowest value (0.87Ω) compared to the values for AuPt_{1/4} and commercial Pt/C (6.34 and 1.54Ω , respectively). By comparing the resistance corresponding to the transfer of electrons (R_2), AuPt_{1/4Cl} shows again the lowest values (2.4Ω) compared to the ones measured for AuPt_{1/4} and Pt/C (9.24 and 17.04Ω , respectively). This indicates efficient

species adsorption and rapid charge transfer in AuPt_{1/4}Cl.

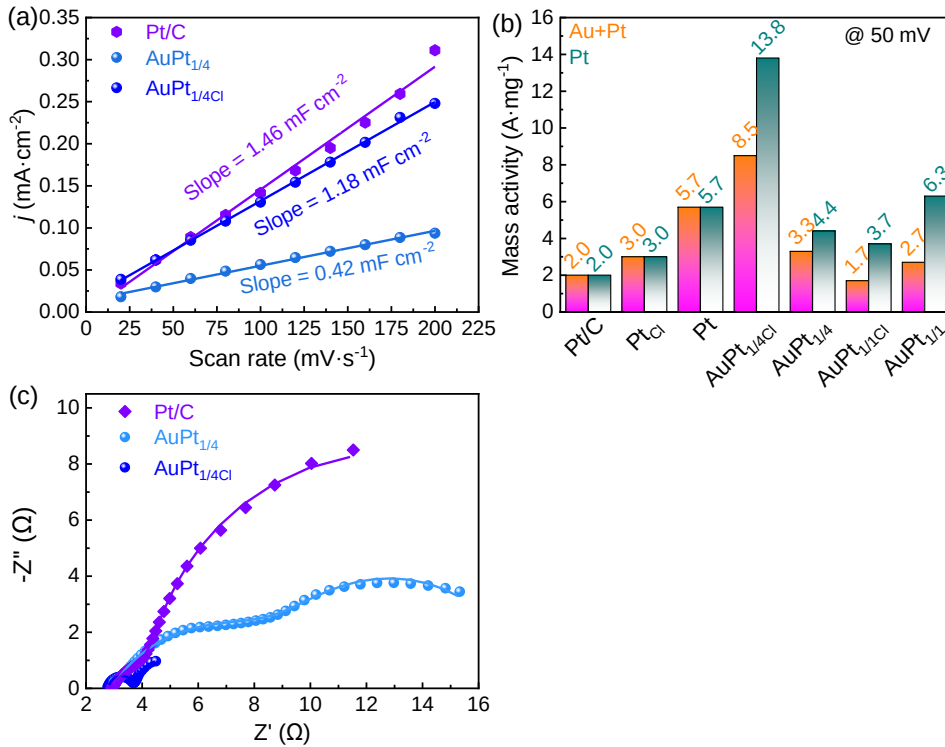


Figure 2.19 (a) Calculation of the electrochemical double layer capacitance (C_{dl}) for commercial Pt/C, AuPt_{1/4}, and AuPt_{1/4}Cl. (b) Mass activities of commercial Pt/C, AuPt_{1/1}, AuPt_{1/1}Cl, AuPt_{1/4}, and AuPt_{1/4}Cl, Pt, and PtCl at the overpotential of 50 mV with the same total loading on the WE. (c) EIS Nyquist plot for commercial Pt/C, AuPt_{1/4}, AuPt_{1/4}Cl.

Table 2.4 Summary of the parameters obtained from the RC equivalent circuit model

Sample	Potential (V vs. RHE)	R_s (Ω)	R_1 (Ω)	R_2 (Ω)	CPE_1	CPE_2
AuPt _{1/4} Cl	-0.013	2.80	0.87	2.40	0.0137	0.9228
AuPt _{1/4}	-0.013	2.88	6.34	9.24	0.0138	0.8017
Pt/C	-0.013	2.94	1.54	17.04	0.0037	0.9867

To corroborate our hypothesis, we ran HER measurements in neutral (1 M potassium phosphate-buffered saline, PBS, pH=7) and alkaline (1 M potassium hydroxide, pH=14) media. As shown in [Figure 2.20](#), in neutral and alkaline solutions, AuPt_{1/4} and AuPt_{1/4}Cl exhibited poorer performance than commercial Pt/C. Remarkably, AuPt_{1/4}Cl exhibits the highest overpotential at 10 mA·cm⁻² in alkaline media, while AuPt_{1/4} showed a better activity close to the one measured for commercial Pt/C ([Table 2.5](#)). This observation proves the crucial role of H⁺ adsorption in the HER performance of AuPt structures and, at the same time, the synergetic effect differences that Au and Pt could play in alkaline

media. The significant improvement of the AuPt_{1/4} NCs from neutral to alkaline media could result from the higher adsorption energy of H⁺ species in Au, thus leading to an improved activity at higher pH.

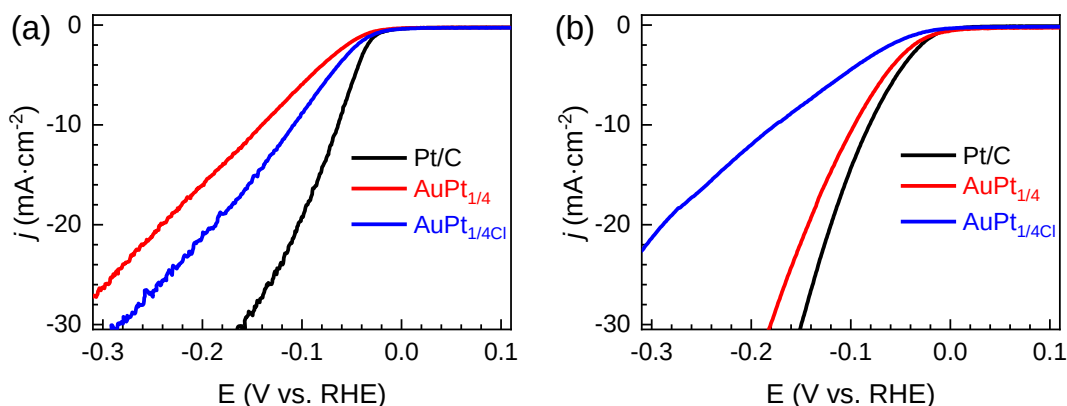


Figure 2.20 LSV curves of Pt/C, AuPt_{1/4}, and AuPt_{1/4Cl} in (a) 1 M potassium phosphate-buffered saline (PBS, pH=7) electrolyte and (b) 1 M potassium hydroxide (pH=14) electrolyte.

Table 2.5 Summary of the overpotentials performance @ 10 mA·cm⁻² for Pt/C, AuPt_{1/4}, and AuPt_{1/4Cl} in 1 M potassium phosphate-buffered saline (PBS, pH=7) and in 1 M potassium hydroxide (pH=14) electrolytes.

Samples	Overpotentials at 10 mA·cm ⁻² (mV)	
	Potassium phosphate-buffered (pH = 7)	Potassium hydroxide (pH = 14)
Pt/C	64	81
AuPt _{1/4}	140	96
AuPt _{1/4Cl}	108	176

2.3.5 Stability measurements and post-characterization for AuPt_{1/4Cl}

Finally, the stability of the AuPt_{1/4Cl} electrocatalyst was evaluated by conducting 2000 and 4000 cycles of CV ([Figure 2.21a](#)) and a chronopotentiometry test ([Figure 2.21b](#)). As observed, the overpotential at 10 mA·cm⁻² does not undergo significant increases, remaining close to 30 mV after 2000 or even 4000 cycles, as shown in the inset image of [Figure 2.21a](#). A slight deviation is observed in the overpotentials at 100 mA·cm⁻², with an increase from 148 mV to 156 mV and 168 mV for 2000 and 4000 cycles,

respectively. Nevertheless, the activity of the $\text{AuPt}_{1/4}\text{Cl}$ electrocatalyst remains relatively stable after 4000 cycles. The chronopotentiometry test was carried out by drop-casting a catalyst ink containing $\text{AuPt}_{1/4}\text{Cl}$ NCs onto a carbon cloth ($1 \times 1.25 \text{ cm}^2$). Chronopotentiometry was run over 200 hours in an H-type cell, maintaining a constant current density of $10 \text{ mA}\cdot\text{cm}^{-2}$ ([Figure 2.21b](#)). Samples show rather good stability with an increase of the overpotential of ca. 5-6% after 200 hours. These results are consistent with the trend observed in [Figure 2.21a](#) and comparable with the reported stabilities for other catalysts ([Table 2.6](#)), indicating good stability of $\text{AuPt}_{1/4}\text{Cl}$ performance over prolonged operating time.

Analysis of the sample after the long stability test confirmed that the structure of a Au-rich core surrounded by a Pt shell was preserved ([Figure 2.22](#)). Noteworthy, XPS analysis confirmed a partial oxidation of the Pt-shell as well as an increase in the Au^{1+} contribution after 200 hours ([Figure 2.23](#)). This increase could be related to a partial migration of Au atoms to the surface that eventually does reduce the catalytic activity.

In summary, after more than 200 hours of continuous operation, the $\text{AuPt}_{1/4}\text{Cl}$ catalyst maintained its morphology and composition with no significant changes observed. This outcome convincingly demonstrates the excellent catalytic durability and structural stability, providing solid experimental evidence and theoretical support for its long-term reliable performance in practical applications. It also highlights the catalyst's strong potential for widespread implementation in industrial catalytic processes.

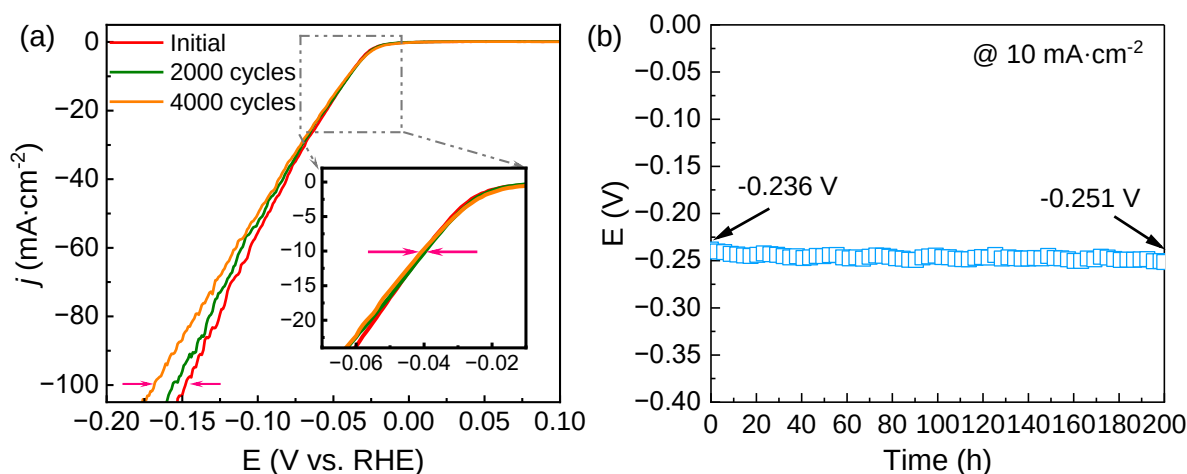


Figure 2.21 (a) Evolution of the stability of $\text{AuPt}_{1/4}\text{Cl}$ by running CV for 2000 and 4000 cycles, respectively. (b) Chronopotentiometry for $\text{AuPt}_{1/4}\text{Cl}$ samples at $10 \text{ mA}\cdot\text{cm}^{-2}$.

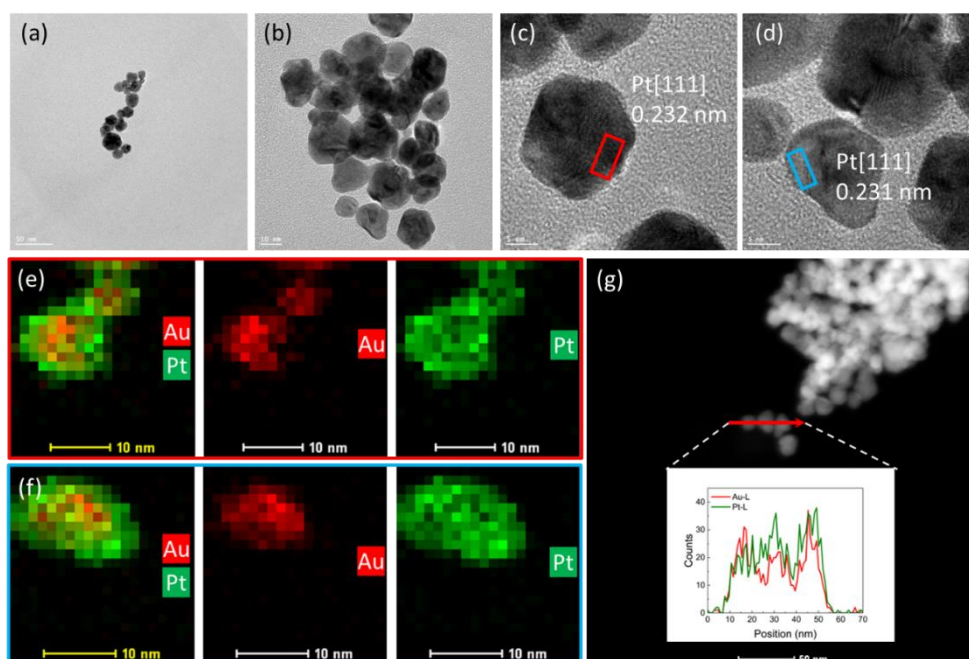


Figure 2.22 Characterizations of AuPt_{1/4}Cl after long term stability measurement: (a-d) TEM and HR-TEM images at different magnifications and measured lattice fringes; (e and f) EDX mapping of different NCs; and (g) Au and Pt composition along a set of NCs (EDX line scanning).

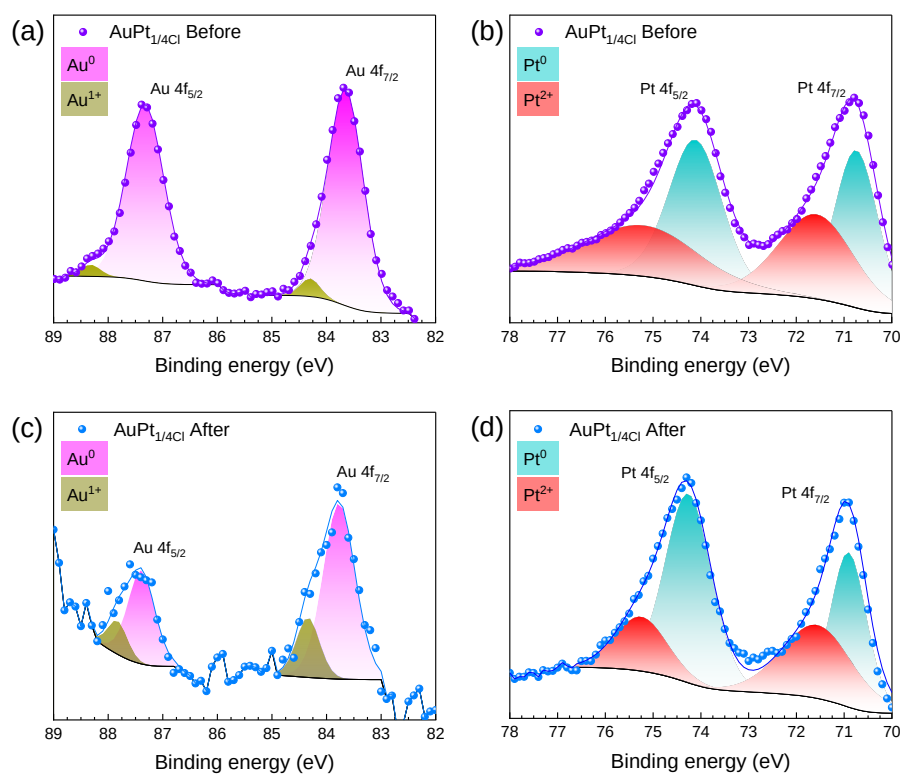


Figure 2.23 High-resolution XPS spectra for AuPt_{1/4}Cl NCs (a, b) before and (c, d) after a chronopotentiometry (200 hours at 10 mA·cm⁻²).

Table 2.6 Summary of the specific data published about stability measurements by running CV cycles or chronoamperometry/chronopotentiometry.

Sample	CV cycles (times)	Chronoamperometry/Chronopotentiometry @10 mA·cm ⁻² (h)	References
AuPt _{1/4} Cl	4000	200	This work
Pt ₅ /HMCS-5.08%	3000	5.56	71
Pt ₁ /NMHCS	3000	10	72
CoSe ₂ /a-CoP	-	50	75
Pd NPs-Bis-24h	10000	40	76
MoP-Ru ₂ P/NPC	-	12	77
E-MoS ₂ -Pt-r	1000	10	78
AuPtPd NPs	1000	2.78	61
Pt-ACs/CoNC	5000	50	65
Pt(110)-Ni ₃ N	-	24	64
CB[8]-Pt	10000	120	30
Pt/P@Cu	1000	20h @20 mA·cm ⁻²	69
PtHCu11 (2)	3000	-	70

- No data provided in the publications

2.4 Conclusions

In summary, we have successfully synthesized a series of AuPt NCs with varying Au:Pt ratios using a fast and facile MW-assisted synthetic approach. The addition of HCl played a pivotal role providing precise control over the structure and morphology of the NCs. Ultimately, AuPt_{1/4}Cl was identified as the most promising candidate for the HER in acidic media demonstrating remarkable electrocatalytic activity despite not having the highest Pt content among all the samples. Precisely, it exhibited overpotentials of 24 mV and 51 mV (at 10 and 100 mA·cm⁻², respectively) and a Tafel slope of 13 mV·dec⁻¹. This excellent performance can be attributed to the distinctive core-shell structure of NCs, wherein a Pt shell wraps the Au core. This configuration maximizes the exposure of Pt atoms to the surrounding environment, surpassing the activity of commercial Pt/C catalysts. Furthermore, synergistic effects between the Au core and the Pt shell likely contribute to superior performance by modulating the electronic structure of the core-shell nanocatalyst. Despite its low Pt content, the AuPt_{1/4}Cl nanocatalyst exhibited a hydrogen production rate significantly higher than that of commercial Pt/C (by 4.25-fold) and surpassed the AuPt_{1/4} counterpart (by 2.6-fold). In this context, the low Pt content combined with the high hydrogen production rate offsets the presence of Au in the NCs. Future research should focus on replacing Au with more cost-effective and abundant elements such as Ag, Ni, Co, or Cu. These findings underscore the successful integration of MW-assisted synthesis and halide ions for the rational design of low-Pt content electrocatalysts with enhanced performance in HER.

2.5 References

- 1 Ueckerdt, F.; Bauer, C.; Dirmaichner, A.; Everall, J.; Sacchi, R.; Luderer, G. Potential and risks of hydrogen-based e-fuels in climate change mitigation. *Nature Climate Change* **2021**, *11* (5), 384-393. <https://doi.org/10.1038/s41558-021-01032-7>.
- 2 Nikolaidis, P.; Poullikkas, A. A comparative overview of hydrogen production processes. *Renewable and Sustainable Energy Reviews* **2016**, *67*, 597-611. <https://doi.org/10.1016/j.rser.2016.09.044>.
- 3 Xu, C.; Zhang, M.; Yin, X.; Gao, Q.; Jiang, S.; Cheng, J.; Kong, X.; Liu, B.; Peng, H.-Q. Recent advances in two-dimensional nanomaterials as bifunctional electrocatalysts for full water splitting. *Journal of Materials Chemistry A* **2023**, *11* (35), 18502-18529. <https://doi.org/10.1039/d3ta02293e>.
- 4 Chatenet, M.; Pollet, B. G.; Dekel, D. R.; Dionigi, F.; Deseure, J.; Millet, P.; Braatz, R. D.; Bazant, M. Z.; Eikerling, M.; Staffell, I.; Balcombe, P.; Shao-Horn, Y.; Schäfer, H. Water electrolysis: from textbook knowledge to the latest scientific strategies and industrial developments. *Chemical Society Reviews* **2022**, *51* (11), 4583-4762. <https://doi.org/10.1039/d0cs01079k>.
- 5 Luo, Y.; Zhang, Z.; Chhowalla, M.; Liu, B. Recent advances in design of electrocatalysts for High-Current-Density water splitting. *Advanced Materials* **2021**, *34* (16), 2108133. <https://doi.org/10.1002/adma.202108133>.
- 6 Saidi, W. A.; Nandi, T.; Yang, T. Designing multinary noble metal-free catalyst for hydrogen evolution reaction. *Electrochemical Science Advances* **2022**, *3* (6), e2100224. <https://doi.org/10.1002/elsa.202100224>.
- 7 Pan, S.; Li, H.; Liu, D.; Huang, R.; Pan, X.; Ren, D.; Li, J.; Shakouri, M.; Zhang, Q.; Wang, M.; Wei, C.; Mai, L.; Zhang, B.; Zhao, Y.; Wang, Z.; Graetzel, M.; Zhang, X. Efficient and stable noble-metal-free catalyst for acidic water oxidation. *Nature Communications* **2022**, *13*, 2294. <https://doi.org/10.1038/s41467-022-30064-6>.
- 8 Zhao, J.; Liao, N.; Luo, J. Transforming NiFe layered double hydroxide into NiFeP_x for efficient alkaline water splitting. *Journal of Materials Chemistry A* **2023**, *11* (17), 9682-9690. <https://doi.org/10.1039/d3ta01192e>.
- 9 Liu, F.; Shi, C.; Guo, X.; He, Z.; Pan, L.; Huang, Z.; Zhang, X.; Zou, J. Rational design of better hydrogen evolution electrocatalysts for water splitting: a review. *Advanced Science* **2022**, *9* (18), 2200307. <https://doi.org/10.1002/advs.202200307>.
- 10 Herbaut, M.; Siaj, M.; Claverie, J. P. Nanomaterials-based water splitting: how far are we from a sustainable solution? *ACS Applied Nano Materials* **2021**, *4* (2), 907-910. <https://doi.org/10.1021/acsnm.1c00246>.
- 11 Jiao, L.; Jiang, H.-L. Metal-organic frameworks for catalysis: Fundamentals and future prospects. *Chinese Journal of Catalysis* **2023**, *45*, 1-5. [https://doi.org/10.1016/s1872-2067\(22\)64193-7](https://doi.org/10.1016/s1872-2067(22)64193-7).
- 12 Li, Y.; Sun, Y.; Qin, Y.; Zhang, W.; Wang, L.; Luo, M.; Yang, H.; Guo, S. Recent advances on water-splitting electrocatalysis mediated by noble-metal-based nanostructured materials. *Advanced Energy Materials* **2020**, *10* (11), 1903120. <https://doi.org/10.1002/aenm.201903120>.
- 13 McCrum, I. T.; Koper, M. T. M. The role of adsorbed hydroxide in hydrogen evolution reaction kinetics on modified platinum. *Nature Energy* **2020**, *5* (11), 891-899. <https://doi.org/10.1038/s41560-020-00710-8>.
- 14 Zhu, S.; Qin, X.; Xiao, F.; Yang, S.; Xu, Y.; Tan, Z.; Li, J.; Yan, J.; Chen, Q.; Chen, M.; Shao, M. The role of ruthenium in improving the kinetics of hydrogen oxidation and evolution reactions of platinum. *Nature Catalysis* **2021**, *4* (8), 711-718. <https://doi.org/10.1038/s41929-021-00663-5>.

- 15 Tymoczko, J.; Calle-Vallejo, F.; Schuhmann, W.; Bandarenka, A. S. Making the hydrogen evolution reaction in polymer electrolyte membrane electrolyzers even faster. *Nature Communications* **2016**, *7*, 10990. <https://doi.org/10.1038/ncomms10990>.
- 16 Nakaya, Y.; Furukawa, S. Catalysis of alloys: classification, principles, and design for a variety of materials and reactions. *Chemical Reviews* **2022**, *123* (9), 5859-5947. <https://doi.org/10.1021/acs.chemrev.2c00356>.
- 17 Liu, J.; Lee, C.; Hu, Y.; Liang, Z.; Ji, R.; Soo, X. Y. D.; Zhu, Q.; Yan, Q. Recent progress in intermetallic nanocrystals for electrocatalysis: from binary to ternary to high-entropy intermetallics. *SmartMat* **2023**, *4* (4), e1210. <https://doi.org/10.1002/smm2.1210>.
- 18 Shi, Y.; Ma, Z.-R.; Xiao, Y.-Y.; Yin, Y.-C.; Huang, W.-M.; Huang, Z.-C.; Zheng, Y.-Z.; Mu, F.-Y.; Huang, R.; Shi, G.-Y.; Sun, Y.-Y.; Xia, X.-H.; Chen, W. Electronic metal-support interaction modulates single-atom platinum catalysis for hydrogen evolution reaction. *Nature Communications* **2021**, *12*, 3021. <https://doi.org/10.1038/s41467-021-23306-6>.
- 19 Zeng, Z.; Kuang, S.; Huang, Z.-F.; Chen, X.; Su, Y.; Wang, Y.; Zhang, S.; Ma, X. Boosting oxygen evolution over inverse spinel Fe-Co-Mn oxide nanocubes through electronic structure engineering. *Chemical Engineering Journal* **2022**, *433*, 134446. <https://doi.org/10.1016/j.cej.2021.134446>.
- 20 Yao, R.; Zhou, Y.; Shi, H.; Wan, W.; Zhang, Q.; Gu, L.; Zhu, Y.; Wen, Z.; Lang, X.; Jiang, Q. Nanoporous surface high-entropy alloys as highly efficient multisite electrocatalysts for nonacidic hydrogen evolution reaction. *Advanced Functional Materials* **2020**, *31* (10), 2009613. <https://doi.org/10.1002/adfm.202009613>.
- 21 Strmcnik, D.; Uchimura, M.; Wang, C.; Subbaraman, R.; Danilovic, N.; Van Der Vliet, D.; Paulikas, A. P.; Stamenkovic, V. R.; Markovic, N. M. Improving the hydrogen oxidation reaction rate by promotion of hydroxyl adsorption. *Nature Chemistry* **2013**, *5* (4), 300-306. <https://doi.org/10.1038/nchem.1574>.
- 22 Lim, C.; Fairhurst, A. R.; Ransom, B. J.; Haering, D.; Stamenkovic, V. R. Role of transition metals in Pt alloy catalysts for the oxygen reduction reaction. *ACS Catalysis* **2023**, *13* (22), 14874-14893. <https://doi.org/10.1021/acscatal.3c03321>.
- 23 Porter, N. S.; Wu, H.; Quan, Z.; Fang, J. Shape-control and electrocatalytic activity-enhancement of Pt-based bimetallic nanocrystals. *Accounts of Chemical Research* **2013**, *46* (8), 1867-1877. <https://doi.org/10.1021/ar3002238>.
- 24 Gao, G.; Zhu, G.; Chen, X.; Sun, Z.; Cabot, A. Optimizing Pt-based alloy electrocatalysts for improved hydrogen evolution performance in alkaline electrolytes: a comprehensive review. *ACS Nano* **2023**, *17* (21), 20804-20824. <https://doi.org/10.1021/acsnano.3c05810>.
- 25 Lu, Y.; Huang, K.; Cao, X.; Zhang, L.; Wang, T.; Peng, D.; Zhang, B.; Liu, Z.; Wu, J.; Zhang, Y.; Chen, C.; Huang, Y. Atomically dispersed intrinsic hollow sites of M-M₁-M (M₁ = Pt, Ir; M = Fe, Co, Ni, Cu, Pt, Ir) on FeCoNiCuPtIr nanocrystals enabling rapid water redox. *Advanced Functional Materials* **2022**, *32* (19), 2110645. <https://doi.org/10.1002/adfm.202110645>.
- 26 Deng, S.; Zhang, B.; Choo, P.; Smeets, P. J. M.; Odom, T. W. Plasmonic photoelectrocatalysis in copper-platinum core-shell nanoparticle lattices. *Nano Letters* **2021**, *21* (3), 1523-1529. <https://doi.org/10.1021/acs.nanolett.0c05029>.
- 27 Chen, Y.; Sun, H.; Gates, B. C. Prototype atomically dispersed supported metal catalysts: iridium and platinum. *Small* **2020**, *17* (16), 2004665. <https://doi.org/10.1002/smll.202004665>.
- 28 Zhou, K. L.; Wang, Z.; Han, C. B.; Ke, X.; Wang, C.; Jin, Y.; Zhang, Q.; Liu, J.; Wang, H.; Yan, H. Platinum single-atom catalyst coupled with transition metal/metal oxide heterostructure for accelerating alkaline hydrogen evolution reaction. *Nature Communications* **2021**, *12*, 3783. <https://doi.org/10.1038/s41467-021-24079-8>.
- 29 Ge, Z.-X.; Ding, Y.; Wang, T.-J.; Shi, F.; Jin, P.-J.; Chen, P.; He, B.; Yin, S.-B.; Chen, Y. Interfacial engineering of holey platinum nanotubes for formic acid electrooxidation boosted

- water splitting. *Journal of Energy Chemistry* **2022**, *77*, 209-216. <https://doi.org/10.1016/j.jechem.2022.10.020>.
- 30 Geng, W.; Song, X.; Wei, Z.; Cao, M.; Cao, R. Ultralow Pt catalyst loading prepared by the electroreduction of a supramolecular assembly for the hydrogen evolution reaction. *ACS Applied Energy Materials* **2022**, *5* (12), 15597-15604. <https://doi.org/10.1021/acsaem.2c03184>.
 - 31 Loza, K.; Heggen, M.; Epple, M. Synthesis, structure, properties, and applications of bimetallic nanoparticles of noble metals. *Advanced Functional Materials* **2020**, *30* (21), 1909260. <https://doi.org/10.1002/adfm.201909260>.
 - 32 Lu, P.; Zhou, J.; Hu, Y.; Yin, J.; Wang, Y.; Yu, J.; Ma, Y.; Zhu, Z.; Zeng, Z.; Fan, Z. Gold-based nanoalloys: synthetic methods and catalytic applications. *Journal of Materials Chemistry A* **2021**, *9* (35), 19025-19053. <https://doi.org/10.1039/d1ta03646g>.
 - 33 Strmcnik, D.; Lopes, P. P.; Genorio, B.; Stamenkovic, V. R.; Markovic, N. M. Design principles for hydrogen evolution reaction catalyst materials. *Nano Energy* **2016**, *29*, 29-36. <https://doi.org/10.1016/j.nanoen.2016.04.017>.
 - 34 Tanaka, S.; Hoshi, N.; Nakamura, M. Hydrogen evolution reaction on AuNi surface alloy formed on single crystal Au electrodes. *ChemElectroChem* **2023**, *10* (16), e202300095. <https://doi.org/10.1002/celec.202300095>.
 - 35 Mott, D.; Luo, J.; Njoki, P. N.; Lin, Y.; Wang, L.; Zhong, C.-J. Synergistic activity of gold-platinum alloy nanoparticle catalysts. *Catalysis Today* **2007**, *122* (3-4), 378-385. <https://doi.org/10.1016/j.cattod.2007.01.007>.
 - 36 Lopes, P. P.; Li, D.; Lv, H.; Wang, C.; Tripkovic, D.; Zhu, Y.; Schimmenti, R.; Daimon, H.; Kang, Y.; Snyder, J.; Becknell, N.; More, K. L.; Strmcnik, D.; Markovic, N. M.; Mavrikakis, M.; Stamenkovic, V. R. Eliminating dissolution of platinum-based electrocatalysts at the atomic scale. *Nature Materials* **2020**, *19* (11), 1207-1214. <https://doi.org/10.1038/s41563-020-0735-3>.
 - 37 Yu, Y.; Lee, S. J.; Theerthagiri, J.; Lee, Y.; Choi, M. Y. Architecting the AuPt alloys for hydrazine oxidation as an anolyte in fuel cell: comparative analysis of hydrazine splitting and water splitting for energy-saving H₂ generation. *Applied Catalysis B: Environment and Energy* **2022**, *316*, 121603. <https://doi.org/10.1016/j.apcatb.2022.121603>.
 - 38 Wang, X.; Qi, J.; Luo, X.; Yang, Z.; Fan, Y.; Jiang, Z.; Liu, C.; Yang, J.; Chen, W. Core-shell Au@PtIr nanowires with dendritic alloy shells as efficient bifunctional catalysts toward methanol oxidation and hydrogen evolution reactions. *International Journal of Hydrogen Energy* **2021**, *46* (74), 36771-36780. <https://doi.org/10.1016/j.ijhydene.2021.08.214>.
 - 39 Cao, Y.; Xiahou, Y.; Xing, L.; Zhang, X.; Li, H.; Wu, C.; Xia, H. Fe(ii)-assisted one-pot synthesis of ultra-small core-shell Au-Pt nanoparticles as superior catalysts towards the HER and ORR. *Nanoscale* **2020**, *12* (39), 20456-20466. <https://doi.org/10.1039/d0nr04995f>.
 - 40 Wan, R.; Luo, M.; Wen, J.; Liu, S.; Kang, X.; Tian, Y. Pt-Co single atom alloy catalysts: accelerated water dissociation and hydrogen evolution by strain regulation. *Journal of Energy Chemistry* **2022**, *69*, 44-53. <https://doi.org/10.1016/j.jechem.2021.12.045>.
 - 41 Germano, L. D.; Marangoni, V. S.; Mogili, N. V. V.; Seixas, L.; Maroneze, C. M. Ultrasmall (<2 nm) Au@Pt Nanostructures: tuning the surface electronic states for electrocatalysis. *ACS Applied Materials & Interfaces* **2019**, *11* (6), 5661-5667. <https://doi.org/10.1021/acsaami.8b12712>.
 - 42 Torras, M.; Roig, A. From silver plates to spherical nanoparticles: snapshots of microwave-assisted polyol synthesis. *ACS Omega* **2020**, *5* (11), 5731-5738. <https://doi.org/10.1021/acsomega.9b03748>.
 - 43 Torras, M.; Roig, A. Copper oxide nanocubes wrapping metals by microwave synthesis. *Crystal Growth & Design* **2021**, *21* (9), 5027-5035. <https://doi.org/10.1021/acs.cgd.1c00462>.
 - 44 Seth, J.; Prasad, B. L. V. Bromide ion mediated modification to digestive ripening process: preparation of ultra-small Pd, Pt, Rh and Ru nanoparticles. *Nano Research* **2016**, *9* (7), 2007-

2017. <https://doi.org/10.1007/s12274-016-1091-0>.
- 45 Huang, X.; Li, Y.; Li, Y.; Zhou, H.; Duan, X.; Huang, Y. Synthesis of PtPd bimetal nanocrystals with controllable shape, composition, and their tunable catalytic properties. *Nano Letters* **2012**, 12 (8), 4265-4270. <https://doi.org/10.1021/nl301931m>.
- 46 Lohse, S. E.; Burrows, N. D.; Scarabelli, L.; Liz-Marzán, L. M.; Murphy, C. J. Anisotropic noble metal nanocrystal growth: the role of halides. *Chemistry of Materials* **2013**, 26 (1), 34-43. <https://doi.org/10.1021/cm402384j>.
- 47 Guardia, P.; Nitti, S.; Materia, M. E.; Pugliese, G.; Yaacoub, N.; Greneche, J. -m.; Lefevre, C.; Manna, L.; Pellegrino, T. Gold-iron oxide dimers for magnetic hyperthermia: the key role of chloride ions in the synthesis to boost the heating efficiency. *Journal of Materials Chemistry B* **2017**, 5 (24), 4587-4594. <https://doi.org/10.1039/c7tb00968b>.
- 48 Lim, J.; Bae, W. K.; Park, K. U.; Borg, L. Z.; Zentel, R.; Lee, S.; Char, K. Controlled synthesis of CdSe tetrapods with high morphological uniformity by the persistent kinetic growth and the halide-mediated phase transformation. *Chemistry of Materials* **2012**, 25 (8), 1443-1449. <https://doi.org/10.1021/cm3035592>.
- 49 Ghosh, S.; Manna, L. The many “Facets” of halide ions in the chemistry of colloidal inorganic nanocrystals. *Chemical Reviews* **2018**, 118 (16), 7804-7864. <https://doi.org/10.1021/acs.chemrev.8b00158>.
- 50 Zhang, X.; Liu, B.; Hu, C.; Chen, S.; Liu, X.; Liu, J.; Chen, F.; Chen, J.; Xie, F. A facile method in removal of PVP ligands from silver nanowires for high performance and reusable SERS substrate. *Spectrochimica Acta Part a Molecular and Biomolecular Spectroscopy* **2019**, 228, 117733. <https://doi.org/10.1016/j.saa.2019.117733>.
- 51 Chen, P.-C.; Liu, M.; Du, J. S.; Meckes, B.; Wang, S.; Lin, H.; Dravid, V. P.; Wolverton, C.; Mirkin, C. A. Interface and heterostructure design in polyelemental nanoparticles. *Science* **2019**, 363 (6430), 959-964. <https://doi.org/10.1126/science.aav4302>.
- 52 Wang, Q.; Jia, W.; Liu, B.; Zhao, W.; Li, C.; Zhang, J.; Xu, G. Controllable synthesis of nearly monodisperse spherical aggregates of CeO₂ nanocrystals and their catalytic activity for HCHO oxidation. *Chemistry - an Asian Journal* **2012**, 7 (10), 2258-2267. <https://doi.org/10.1002/asia.201200432>.
- 53 Coviello, V.; Forrer, D.; Amendola, V. Recent developments in plasmonic alloy nanoparticles: synthesis, modelling, properties and applications. *ChemPhysChem* **2022**, 23 (21), e202200136. <https://doi.org/10.1002/cphc.202200136>.
- 54 Amendola, V.; Pilot, R.; Frascioni, M.; Maragò, O. M.; Iatì, M. A. Surface plasmon resonance in gold nanoparticles: a review. *Journal of Physics Condensed Matter* **2017**, 29 (20), 203002. <https://doi.org/10.1088/1361-648x/aa60f3>.
- 55 Rodríguez-Fernández, J.; Pérez-Juste, J.; De Abajo, F. J. G.; Liz-Marzán, L. M. Seeded growth of submicron Au colloids with quadrupole plasmon resonance modes. *Langmuir* **2006**, 22 (16), 7007-7010. <https://doi.org/10.1021/la060990n>.
- 56 Loiudice, A.; Buonsanti, R. Reaction intermediates in the synthesis of colloidal nanocrystals. *Nature Synthesis* **2022**, 1 (5), 344-351. <https://doi.org/10.1038/s44160-022-00056-x>.
- 57 Fan, Q.; Liu, K.; Liu, Z.; Liu, H.; Zhang, L.; Zhong, P.; Gao, C. A ligand-exchange route to noble metal nanocrystals with a clean surface for enhanced optical and catalytic properties. *Particle & Particle Systems Characterization* **2017**, 34 (8), 1700075. <https://doi.org/10.1002/ppsc.201700075>.
- 58 Seh, Z. W.; Kibsgaard, J.; Dickens, C. F.; Chorkendorff, I.; Nørskov, J. K.; Jaramillo, T. F. Combining theory and experiment in electrocatalysis: Insights into materials design. *Science* **2017**, 355 (6321), 147. <https://doi.org/10.1126/science.aad4998>.
- 59 Rakočević, L.; Simatović, I. S.; Maksić, A.; Rajić, V.; Štrbac, S.; Srejić, I. PtAu nanoparticles supported by reduced graphene oxide as a highly active catalyst for hydrogen evolution.

Catalysts **2021**, *12* (1), 43. <https://doi.org/10.3390/catal12010043>.

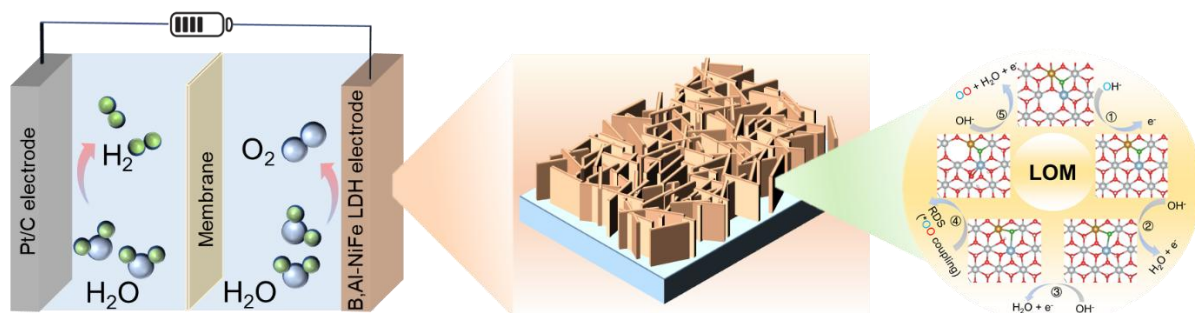
- 60 Feng, J.-J.; Liu, L.; Ma, X.; Yuan, J.; Wang, A.-J. Ultrasonication-assisted wet-chemical fabrication of uniform AuPt nanodendrites as efficient electrocatalyst for oxygen reduction and hydrogen evolution reactions. *International Journal of Hydrogen Energy* **2016**, *42* (4), 2071-2080. <https://doi.org/10.1016/j.ijhydene.2016.11.019>.
- 61 Chen, H.-Y.; Wang, A.-J.; Zhang, L.; Yuan, J.; Zhang, Q.-L.; Feng, J.-J. One-pot wet-chemical synthesis of uniform AuPtPd nanodendrites as efficient electrocatalyst for boosting hydrogen evolution and oxygen reduction reactions. *International Journal of Hydrogen Energy* **2018**, *43* (49), 22187-22194. <https://doi.org/10.1016/j.ijhydene.2018.10.120>.
- 62 Qu, Y.; Yu, Z.; Wei, D.; Chen, L.; Zheng, Z.; Xiao, N.; Wang, L.; Yu, J. PVA decorated Pt nanoparticles as an efficient electrocatalyst for hydrogen evolution reaction. *Ionics* **2021**, *27* (11), 4885-4895. <https://doi.org/10.1007/s11581-021-04209-4>.
- 63 Zhu, J.; Tu, Y.; Cai, L.; Ma, H.; Chai, Y.; Zhang, L.; Zhang, W. Defect-assisted anchoring of Pt single atoms on MoS₂ nanosheets produces high-performance catalyst for industrial hydrogen evolution reaction. *Small* **2021**, *18* (4), 2104824. <https://doi.org/10.1002/smll.202104824>.
- 64 Qiao, S.; He, Q.; Zhou, Q.; Zhou, Y.; Xu, W.; Shou, H.; Cao, Y.; Chen, S.; Wu, X.; Song, L. Interfacial electronic interaction enabling exposed Pt(110) facets with high specific activity in hydrogen evolution reaction. *Nano Research* **2022**, *16* (1), 174-180. <https://doi.org/10.1007/s12274-022-4654-2>.
- 65 Zhao, Y.; Kumar, P. V.; Tan, X.; Lu, X.; Zhu, X.; Jiang, J.; Pan, J.; Xi, S.; Yang, H. Y.; Ma, Z.; Wan, T.; Chu, D.; Jiang, W.; Smith, S. C.; Amal, R.; Han, Z.; Lu, X. Modulating Pt-O-Pt atomic clusters with isolated cobalt atoms for enhanced hydrogen evolution catalysis. *Nature Communications* **2022**, *13*, 2430. <https://doi.org/10.1038/s41467-022-30155-4>.
- 66 Zhang, Y.; Liu, L.; Sun, C.; Du, Y.; Zhou, Y.; Xie, Q. NaBH₄-electrooxidation mediated electrodeposition of catalytic Pt nanoparticles on a honeycomb-gold electrode for hydrogen evolution reaction. *Journal of Alloys and Compounds* **2021**, *888*, 161564. <https://doi.org/10.1016/j.jallcom.2021.161564>.
- 67 Yi, M.; Li, N.; Lu, B.; Li, L.; Zhu, Z.; Zhang, J. Single-atom Pt decorated in heteroatom (N, B, and F)-doped ReS₂ Grown on Mo₂CT_x for efficient pH-universal hydrogen evolution reaction and flexible Zn-air batteries. *Energy Storage Materials* **2021**, *42*, 418-429. <https://doi.org/10.1016/j.ensm.2021.07.048>.
- 68 Yu, F.-Y.; Lang, Z.-L.; Yin, L.-Y.; Feng, K.; Xia, Y.-J.; Tan, H.-Q.; Zhu, H.-T.; Zhong, J.; Kang, Z.-H.; Li, Y.-G. Pt-O bond as an active site superior to Pt0 in hydrogen evolution reaction. *Nature Communications* **2020**, *11*, 490. <https://doi.org/10.1038/s41467-019-14274-z>.
- 69 Tan, Y.; Liu, L.; Zhang, L.; Zhao, S.; Brett, D. J. L.; Shearing, P. R.; Bai, Y.; Parkin, I. P.; He, G. Phosphorus-modified Pt@Cu surfaces for efficient electrocatalysis of hydrogen evolution. *Materials Advances* **2022**, *3* (20), 7667-7672. <https://doi.org/10.1039/d2ma00772j>.
- 70 Silalahi, R. P. B.; Liang, H.; Jo, Y.; Liao, J.; Chiu, T.; Wu, Y.; Wang, X.; Kahlal, S.; Wang, Q.; Choi, W.; Lee, D.; Saillard, J.; Liu, C. W. Hydride-containing Pt-doped Cu-rich nanoclusters: synthesis, structure, and electrocatalytic hydrogen evolution. *Chemistry - a European Journal* **2023**, *30* (13), e202303755. <https://doi.org/10.1002/chem.202303755>.
- 71 Wan, X.; Wu, H. B.; Guan, B. Y.; Luan, D.; Lou, X. W. Confining sub-nanometer Pt clusters in hollow mesoporous carbon spheres for boosting hydrogen evolution activity. *Advanced Materials* **2019**, *32* (7), 1901349. <https://doi.org/10.1002/adma.201901349>.
- 72 Kuang, P.; Wang, Y.; Zhu, B.; Xia, F.; Tung, C.; Wu, J.; Chen, H. M.; Yu, J. Pt single atoms supported on N-doped mesoporous hollow carbon spheres with enhanced electrocatalytic H₂-evolution activity. *Advanced Materials* **2021**, *33* (18), 2008599. <https://doi.org/10.1002/adma.202008599>.
- 73 Choi, J.; Lee, Y.; Kim, J.; Lee, H. Enhancing stability of octahedral PtNi nanoparticles for oxygen reduction reaction by halide treatment. *Journal of Power Sources* **2016**, *307*, 883-890.

<https://doi.org/10.1016/j.jpowsour.2016.01.063>.

- 74 Guo, Y.; Hou, B.; Cui, X.; Liu, X.; Tong, X.; Yang, N. Pt atomic layers boosted hydrogen evolution reaction in nonacidic media. *Advanced Energy Materials* **2022**, 12 (43), 2201548. <https://doi.org/10.1002/aenm.202201548>.
- 75 Shen, S.; Wang, Z.; Lin, Z.; Song, K.; Zhang, Q.; Meng, F.; Gu, L.; Zhong, W. Crystalline-amorphous interfaces coupling of CoSe₂/CoP with optimized d-band center and boosted electrocatalytic hydrogen evolution. *Advanced Materials* **2022**, 34 (13), 2110631. <https://doi.org/10.1002/adma.202110631>.
- 76 Cheng, H.; Yang, N.; Liu, G.; Ge, Y.; Huang, J.; Yun, Q.; Du, Y.; Sun, C.; Chen, B.; Liu, J.; Zhang, H. Ligand-exchange-induced amorphization of Pd nanomaterials for highly efficient electrocatalytic hydrogen evolution reaction. *Advanced Materials* **2020**, 32 (11), 1902964. <https://doi.org/10.1002/adma.201902964>.
- 77 Gao, Y.; Chen, Z.; Zhao, Y.; Yu, W.; Jiang, X.; He, M.; Li, Z.; Ma, T.; Wu, Z.; Wang, L. Facile synthesis of MoP-Ru₂P on porous N, P co-doped carbon for efficiently electrocatalytic hydrogen evolution reaction in full pH range. *Applied Catalysis B: Environment and Energy* **2021**, 303, 120879. <https://doi.org/10.1016/j.apcatb.2021.120879>.
- 78 He, S.; Liu, Y.; Li, H.; Wu, Q.; Ma, D.; Gao, D.; Bi, J.; Yang, Y.; Cui, C. Highly dispersed Mo sites on Pd nanosheets enable selective ethanol-to-acetate conversion. *ACS Applied Materials & Interfaces* **2021**, 13 (11), 13311-13318. <https://doi.org/10.1021/acsami.1c01010>.

Chapter 3

Tailoring the Lattice Oxygen Reactivity in NiFe Layered Double Hydroxides via B and Al Dual-heteroatom Doping



The results presented in this chapter are part of a manuscript to be submitted, entitled “*Tailoring the lattice oxygen reactivity in NiFe layered double hydroxides via B and Al dual-heteroatom doping*” by Xuesong Zhang, Pablo Guardia, et al. A tentative exploitation plan for these findings is included in Chapter 3. The authors would like to acknowledge the collaboration with Scientific Compass, China (www.shiyanjia.com) for the DFT simulation. The synthesis, experimental characterization, and analysis were carried out by the candidate.

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Chapter Summary

Developing cost-effective, high-performance electrocatalysts for the oxygen evolution reaction (OER) is crucial for advancing sustainable green hydrogen production. Herein, we report a dual-heteroatom-doped NiFe layered double hydroxide (B,Al-NiFe LDH) catalyst to fine-tune their electronic structure and enhance catalytic activity. This optimized catalyst achieves remarkable OER performance, requiring ultra-low overpotentials of 169, 196, and 254 mV at current densities of 10, 100, and 500 mA·cm⁻², respectively. It features a low Tafel slope of 38.6 mV·dec⁻¹, a large electrochemical active surface area (ECSA) of 254.50 cm², and a high turnover frequency (TOF) of 2.05 s⁻¹, surpassing many state-of-the-art electrocatalysts. Combined experimental and theoretical investigations reveal that the co-doping of B and Al synergistically tailors the oxidation states of Ni and Fe, alters local bonding environments, promotes lattice oxygen participation, and lowers the energy barrier for oxygen-oxygen (O-O) coupling, thereby favoring the lattice oxygen mechanism (LOM). Notably, in alkaline natural seawater, the catalyst maintains a stable current density of 100 mA·cm⁻² at an overpotential of only 250 mV for over 360 hours of continuous operation. Furthermore, when integrated into a full electrolyzer (B,Al-NiFe||Pt/C), the system achieves a 400 mV reduction in required potential at 400 mA·cm⁻² compared to the benchmark RuO₂||Pt/C configuration. This work highlights the crucial role of co-dopants in tuning catalytic properties and provides a promising strategy for designing next-generation electrocatalysts for efficient freshwater and seawater electrolysis.

3.1 Introduction

The large-scale production of hydrogen represents a key milestone toward a decarbonized and sustainable economy.¹ However, the sluggish kinetics of the oxygen evolution reaction (OER) involving a complex four-electron transfer process severely constrain the overall efficiency of water electrolysis.² Noteworthy, noble metal oxides such as IrO₂ and RuO₂ are considered as benchmark OER catalysts, whose high cost and scarcity further compromise the large-scale production of hydrogen.³

According to the literature, it has been well established that in noble metal oxide catalysts, the adsorbate evolution mechanism (AEM) is dominant in the OER.^{4,5} In the AEM, surface-adsorbed intermediates (*i.e.*, *OH, *O, and *OOH) undergo sequential adsorption and oxidation steps, finally leading to O₂ releasing, as discussed detailly in **Section 1.3.2**.⁶ However, the intrinsic linear scaling relationship between *OH and *OOH intermediates imposes a theoretical minimum overpotential of ~370 mV, which inherently limits the catalytic efficiency achievable.

To overcome the thermodynamic bottleneck, growing evidence has highlighted the lattice oxygen mechanism (LOM) as an alternative reaction pathway able to enhance OER activity.⁷ Unlike AEM, LOM enables direct oxygen-oxygen (O-O) coupling involving lattice oxygen atoms, effectively bypassing the thermodynamic bottleneck associated with the *OH-*OOH scaling relationship and hence reducing the overpotential below ~370 mV. As mentioned in **Section 1.3.2**, recent studies using in situ/operando X-ray absorption spectroscopy (XAS), differential electrochemical mass spectrometry (DEMS), and isotope-labeling techniques have confirmed the participation of lattice oxygen in OER processes on several transition metal (oxy)hydroxides.⁷ Most relevant, this alternative pathway seems to be particularly dominant in transition metal oxides and hydroxides, unlocking the potential of earth-abundant catalysts for OER, paving the way for cost-effective and high-efficiency water electrolysis.⁸

Transition-metal layered double hydroxides (LDH), particularly NiFe LDH, have emerged as prominent candidates owing to their intrinsic high catalytic activity, tunable electronic structures, robust structural stability, and earth-abundant nature.⁹ Moreover, LDH catalysts tend to catalyze the OER via the LOM, which has garnered increasing attention for its potential to enhance reaction kinetics.¹⁰ Nonetheless, NiFe LDH still faces several challenges: its catalytic activity heavily depends on the Ni and Fe active centers, its relatively low electronic conductivity limits performance at high current densities, and metal dissolution under harsh anodic potentials compromises long-term stability.^{11–13} Additionally, their application in seawater electrolysis as a practical and sustainable approach remains limited due to competing side reactions and ion fouling in complex ionic environments.

To overcome these limitations, heteroatom co-doping strategies have been widely investigated to modulate the electronic structure of NiFe LDH, thereby enhancing both catalytic activity and stability. Such strategies typically involve inducing lattice distortions, promoting oxidation of metal centers to higher valence states,¹⁴ optimizing interactions between active sites and oxygen intermediates,¹⁵ and introducing oxygen vacancies (O_v) to accelerate reaction kinetics.¹⁶ In particular, doping with transition metals (*e.g.*, Ru,¹⁷ V,¹⁸ Mo¹⁹) or nonmetals (*e.g.*, P,²⁰ S,²⁰ N²¹) has proven effectively in tuning the d-band center, improving charge redistribution, and enhancing electrical conductivity. These optimizations facilitate lattice oxygen participation in the LOM pathway and improve overall OER performance under harsh conditions.

While many mono-doping strategies have been explored, dual-heteroatom doping remains underexplored, yet holds great potential for synergistically enhancing both the electronic structure and catalytic durability of NiFe LDH. In particular, incorporation Al and B have been demonstrated to significantly alter the local coordination environment and electronic structure of NiFe LDH, ultimately improving OER performance.^{22–24} Notably, B doping, attributed to its high electronegativity (2.04), substitutes bridging

hydroxyl groups and forms metal-boron (M-B) bonds. This replacement induces local electron redistribution and charge polarization, particularly around adjacent metal and oxygen atoms, thereby modulating the electronic structure and indirectly enhancing metal-oxygen (M-O) hybridization. This modification stabilizes key reaction intermediates, such as $^*\text{OH}$, $^*\text{O}$, and $^*\text{OOH}$, thereby improving both catalytic rates and stability.^{24–26} Different from B, Al doping confers enhanced structural stability under alkaline conditions by forming a protective $\text{Al}(\text{OH})_x$ layer, which mitigates metal dissolution and preserves catalyst integrity.²² The synergistic effect of B and Al co-doping further optimizes the lattice oxygen reactivity, enhancing bond strength and structural robustness.

However, systematic studies on the dual-doping effects of nonmetal (B) and main-group metal (Al) in NiFe LDH remain scarce, and their cooperative role in modulating lattice oxygen reactivity, especially under complex environments such as seawater electrolysis, where chloride ions (Cl^-) and multivalent metal cations present considerable challenges. Under high anodic potentials, Cl^- oxidation competes with OER, resulting in catalyst poisoning and structural degradation.^{27,28} Additionally, precipitation of Ca^{2+} and Mg^{2+} ions on electrode surfaces, further compromises catalytic activity.²⁹ Developing a co-doping strategy that addresses these challenges is thus of both fundamental and practical significance.

Building on these insights, we investigate the influence of dual B and Al heteroatom incorporation on the electronic structure, catalytic performance and stability of NiFe LDH. Through combined experimental and mechanistic investigations, we reveal how B and Al dopants modulate metal oxidation states, electron density distribution, thereby facilitating the LOM pathway and reducing OER energy barriers. Specifically, Al incorporation optimizes the coordination environment and enhances structural stability, while B stabilizes the structure intermediates and promotes O-O coupling, collectively enhancing lattice oxygen involvement, reducing energy barriers, and improving overall

OER activity. The synergistic co-doping strategy substantially improves the stability of NiFe LDH, particularly under seawater electrolysis conditions, overcoming challenges posed by corrosive Cl^- ions and multivalent metal cations fouling. This work highlights the value of rational heteroatom co-doping design for developing robust and efficient OER catalysts in complex electrochemical environments.

3.2 Experimental

3.2.1 Materials

Nickel(II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, EMSURE® ACS), iron(III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, ACS reagent, $\geq 98\%$), aluminum(III) nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, ACS reagent, $\geq 98\%$), gallium(III) nitrate hydrate ($\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, 99.9% trace metals basis), indium(III) nitrate hydrate ($\text{In}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, 99.9% trace metals basis), ammonium fluoride (NH_4F , ACS reagent, $\geq 98.0\%$), urea (ACS reagent, 99.0-100.5%), sodium borohydride (NaBH_4 , ReagentPlus, 99.0%), sodium hydroxide (NaOH , ACS reagent, $\geq 97.0\%$, pellets), potassium hydroxide (KOH , ACS reagent, $\geq 85.0\%$, pellets), ruthenium(IV) oxide (RuO_2 , 99.9% trace metals basis), hydrochloric acid (HCl , 37%, ACS reagent), Nafion 117 solution ($\sim 5\%$ in a mixture of low aliphatic alcohols), tetramethylammonium hydroxide solution (TMAOH, 25% in water), and 2-propanol ($\geq 99.5\%$) were purchased from Sigma-Aldrich. Commercial Pt/C catalyst (20 wt% of Pt loading) was purchased from Quintech. All reagents were used as received without further purification. Milli-Q water ($18.2 \text{ M}\Omega \cdot \text{cm}$, Milli-Q IQ, Merck Millipore) was used for all the experiments and solutions, except seawater experiments. Nickel foam (NF, 1.5 mm thickness, 110 ppi) was supplied by Suzhou Jiashide Porous Metal Co., Ltd.

3.2.2 Hydrothermal Synthesis of NiFe LDH-based Catalysts

Synthesis of Al-NiFe LDH

Nanosheets were grown on top of a 1.5 mm thick NF substrate ($3 \times 3 \text{ cm}^2$) via a hydrothermal method following a previous reported procedure under optimized conditions.³⁰ First, the NF substrate was cleaned by immersion in an HCl aqueous solution (2 M) at room temperature for 15 minutes with sonication. Afterwards, the NF substrate was thoroughly rinsed with MQ-water, ethanol several times, and dried in a vacuum at 60°C . For the synthesis of Al-NiFe LDH nanosheets, a precursor solution

was prepared by dissolving 1.68 mmol of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.56 mmol of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and 0.07 mmol of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 35 mL Milli-Q water under magnetic stirring for 30 min. Then, 8 mmol of NH_4F and 20 mmol of urea were added sequentially under continuous stirring. After full dissolution of the reactants, the resultant mixture was transferred into a 50-mL Teflon-lined autoclave, and the cleaned NF substrate was vertically immersed in the precursor solution. Finally, the reactor was sealed, placed inside a forced convection at 120 °C, and kept for 6 hours. After the reaction, the NF substrate was rinsed repeatedly with Milli-Q water and dried overnight in a vacuum oven at 60 °C. The final sample was labeled as $\text{Al}_{0.125}\text{-NiFe LDH}$ (see [Figure 3.1](#)). The amount of Al precursor was further tuned from 0.14 to 0.56 mmol, providing samples with different Al compositions. In particular, $\text{Al}_{0.25}\text{-NiFe LDH}$, $\text{Al}_{0.5}\text{-NiFe LDH}$, and $\text{Al}_1\text{-NiFe LDH}$, respectively.

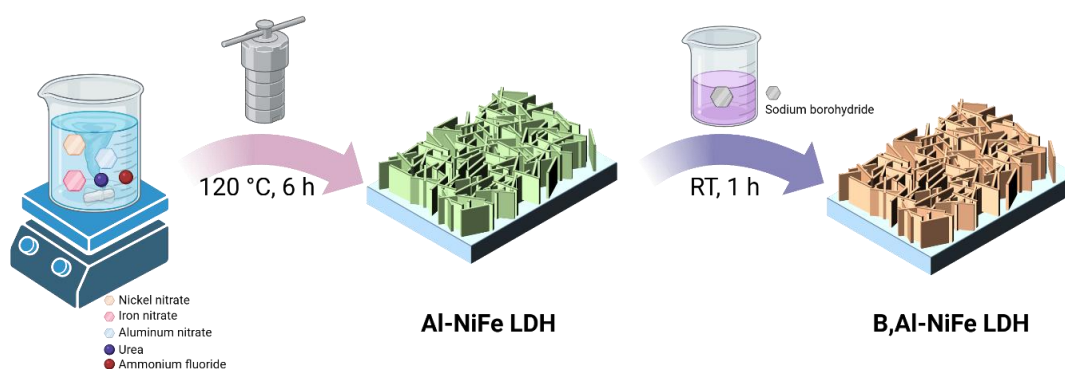


Figure 3.1 The schematic diagram of the reaction process of B,Al-NiFe LDH

Synthesis of M-NiFe LDH

Ga- and In-NiFe LDH catalysts were synthesized following the same method as Al-NiFe LDH, but adding 0.07 mmol of $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ or $\text{In}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ precursors for replacing $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, respectively. Samples were labeled as Ga-NiFe LDH and In-NiFe LDH, respectively.

Synthesis of NiFe LDH

A control sample was produced by following the above procedure but removing $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ from the precursor solution. Briefly, 1.68 mmol of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and 0.56 mmol of $\text{Fe}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ were mixed in 35 mL Milli-Q water under magnetic stirring. Then, 8 mmol of NH_4F and 20 mmol of urea were added sequentially under continuous stirring. The remaining steps were carried out as previously described for $\text{Al}_{0.125}\text{-NiFe}$ LDH sample. After washing and drying, the final product was labeled as NiFe LDH.

Synthesis of B-doped M-NiFe LDH

The B-doped samples were synthesized via a chemical reduction procedure adapted from the literature with minor modifications.²³ In particular, 12.5 mmol of NaOH and 25 mmol of NaBH_4 were dissolved in 50 mL Milli-Q water under magnetic stirring for 20 min. Afterwards, a NF coated with M-NiFe LDH nanosheets was immersed in this solution at room temperature for 1 hour to facilitate boron incorporation. For instance, a $\text{Al}_{0.125}\text{-NiFe}$ LDH was produced with 0.07 mmol of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as shown in [Figure 3.1](#). Subsequently, the resulting samples was rinsed several times with Milli-Q water and ethanol to remove the residual reactants. The final sample was dried under vacuum at 60 °C overnight and labeled as B,Al-NiFe LDH. The same procedure was repeated, but immersing Ga-NiFe LDH or In-NiFe LDH instead of $\text{Al}_{0.125}\text{-NiFe}$ LDH into the NaBH_4 aqueous solution for 1 hour at room temperature. The final samples were labeled as B,Ga-NiFe LDH, and B,In-NiFe LDH, respectively.

Finally, a B-doped NiFe LDH nanosheet sample was prepared by immersing a NiFe-LDH NF substrate into a NaBH_4 aqueous solution for 1 hour at room temperature. The washing procedure was identical to that described previously for B,Al-NiFe LDH, and the resulting sample was labeled as B-NiFe LDH.

Preparation of RuO₂ and Pt/C coated NF

First, RuO₂ or Pt/C catalyst inks were prepared by mixing 750 μl of isopropanol, 220 μl of Milli-Q water, and 30 μl of Nafion solution with 25 mg of RuO₂ or 10 mg of Pt/C, respectively. The mixtures were sonicated for 2 hours to ensure homogeneous dispersion. Finally, 200 μl of the prepared inks were drop-casted onto NF substrates ($1 \times 1 \text{ cm}^2$) and dried on the heating plate at 60 °C. The final catalyst loadings were 5 and 2 $\text{mg}\cdot\text{cm}^{-2}$ for RuO₂ and Pt/C, respectively.

3.2.3 NCs Characterization

X-ray Diffraction (XRD)

Patterns were collected using a conventional Cu-K α radiation source ($\lambda = 1.5406 \text{ \AA}$) in a Bruker ADVANCE D8 employing a Bragg–Brentano geometry. The intensity was recorded within the 2θ range from 5 to 80° at a scanning step of $0.02^\circ\cdot\text{s}^{-1}$.

Scanning Electron Microscopy (SEM)

SEM micrographs were acquired using a Quanta 200 ESEM FEG from FEI under high vacuum at 15.00 kV. Samples were placed on top of carbon tape without further preparation.

Transmission Electron Microscopy (TEM)

Low-resolution electron micrographs were obtained using a JEOL 1210 transmission electron microscope operating at 120 kV, equipped with a side-entry 60°/30° double tilt GATAN 646 specimen holder. HR-TEM, high-angle annular dark-field scanning TEM (HAADF-STEM) images, and energy dispersive X-ray spectroscopy (EDX) mapping were conducted by a Spectra 300 (S)TEM operated at 300 kV (Thermo Fisher). Samples were prepared by sonicating modified NF substrates in ethanol for 30 minutes,

then drop-cast onto a lacey carbon-coated Cu-grids (400 mesh).

X-ray Photoelectron Spectroscopy (XPS)

XPS measurements were acquired in a SPECS PHOIBOS 150 hemispherical energy analyzer using Al K α X-ray radiation (1486.6 eV) for excitation. The powder was drop-cast onto a silica wafer in order to eliminate the influence of the NF substrate.

Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-OES)

To determine the real Ni, Fe, and dopants (B, Al) ratio, ICP-OES was carried out using an Agilent model 5900. The samples were prepared by digesting ~1 mg of NCs in 1 mL of aqua regia for 30 min, then diluting 10 mL with Milli-Q water.

Contact Angle Measurement

The surface wettability of the sample was assessed using a DSA 100 from KRÜSS goniometer. Static contact angles were measured with deionized water droplets of 5 μ L at room temperature. For each modified NF substrate, 3 droplets were placed at different locations, and the contact angle was recorded once the droplet profile remained stable.

3.2.4 Electrochemical Characterization

Electrochemical measurements were carried out in a Bio-Logic VMP3 multichannel potentiostat with a conventional three-electrode configuration. The modified NFs (geometric area: $0.5 \times 1 \text{ cm}^2$) were directly used as the working electrodes (WEs), a platinum mesh as the counter electrode (CE), and a Hg/HgO electrode as the reference electrode (RE). Before testing, catalysts were activated by cyclic voltammetry (CV) at a sweeping rate of $50 \text{ mV} \cdot \text{s}^{-1}$ for 60 cycles in a 1 M KOH electrolyte (pH=14).

The OER activities for each sample were evaluated through linear sweep voltammetry (LSV) at a rate of $5 \text{ mV}\cdot\text{s}^{-1}$, recording three consecutive scans for accuracy. Finally, chronopotentiometry (CP) measurements were conducted at a constant current density of $100 \text{ mA}\cdot\text{cm}^{-2}$ at room temperature.

The alkaline seawater electrolyte was prepared by dissolving 1 M KOH into natural seawater (collected from Barceloneta Beach, Barcelona, Mediterranean Sea, pH=13.8), followed by removal of precipitated salts. Electrochemical measurements followed the same protocols as freshwater.

All potentials were corrected for 90% iR compensation and referenced to the reversible hydrogen electrode (RHE) using $E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.059\cdot\text{pH} + 0.098 \text{ V}$, where the pH values were determined by a pH meter. Tafel slopes were derived from LSV curves following the equation: $\eta = b\cdot\log j + c$, where b is the Tafel slope, η is the overpotential, and j is the current density. Electrochemical double-layer capacitance (C_{dl}) was calculated from CV scans in the non-Faradaic region (0.3 - 0.5 V vs. Hg/HgO) at different scan rates (from 20 to $100 \text{ mV}\cdot\text{s}^{-1}$) with: $C_{\text{dl}} = \Delta j/v$, where $\Delta j = (j_{\text{a}} - j_{\text{c}})/2$ is the current density (at 0.4 V vs. Hg/HgO, $\text{mA}\cdot\text{cm}^{-2}$) and v is the scan rate ($\text{mV}\cdot\text{s}^{-1}$). The ECSA was calculated as $\text{ECSA} = C_{\text{dl}}/C_{\text{s}}$, where the general specific capacitance (C_{s}) is $0.04 \text{ mF}\cdot\text{cm}^{-2}$. Electrochemical impedance spectroscopy (EIS) was acquired with an amplitude of 10 mV at frequencies ranging from 10^6 to 10^{-2} Hz. The turnover frequency (TOF) was calculated as: $\text{TOF} = I/(\alpha\cdot nF)$, where I is current, α is the number of transferred electrons corresponding to a half-reaction that produces a molecular target product ($\alpha = 4$ for OER), n is the active sites number and F is the Faraday constant.

3.2.5 Fabrication and Operation of Anion Exchange Membrane Water/Seawater Electrolyzer Single Cells

Membrane electrode assemblies (MEAs) with 1.0 cm^2 active area were prepared by sandwiching a Nafion 117 membrane between the B,Al-NiFe LDH anode and the drop-

cast Pt/C cathode (B,Al-NiFe||Pt/C). For comparison, a RuO₂ anode was used, resulting in a RuO₂||Pt/C sandwich structure.

Electrolyte circulation (1 M KOH in freshwater or seawater) was maintained at 1.0 mL·s⁻¹ through the anode and cathode compartments via peristaltic pumps. Before testing, MEAs were activated by CV at 100 mV·s⁻¹ for 60 cycles.

Polarization curves were acquired via LSV at 5 mV·s⁻¹ with three independent measurements for statistical reliability. Stability test of the cells was performed by CP at 100 mA·cm⁻² at room temperature for 300 hours.

3.2.6 Computational Methods

Density functional theory (DFT) calculations were performed using the Vienna Ab Initio Simulation Package (VASP), based on first-principles methods.^{31,32} The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional was employed to describe the exchange-correlation effects.³³ The interactions between ionic cores and valence electrons were treated using the projector augmented wave (PAW) method, with a plane-wave basis set and a kinetic energy cutoff of 450 eV.^{34,35}

Partial occupancies of the Kohn-Sham orbitals were handled using the Gaussian smearing method with a smearing width of 0.05 eV. For the optimization of both geometry and lattice size, the Brillouin zone integration was performed with a 1 × 1 × 1 gamma-centered sampling.³⁶ The self-consistent field (SCF) calculations were considered as converged when the total energy difference between iterations was less than 10⁻⁵ eV. Atomic structures were fully relaxed until the maximum residual force on each atom was below 0.02 eV·Å⁻¹.

To eliminate spurious interactions between periodic images, a vacuum layer of 17 Å was introduced perpendicular to the surface. Long-range van der Waals interactions were accounted for using the DFT-D3 method with Grimme's dispersion

corrections.^{37,38} Spin polarization was included to account for magnetic effects.

Gibbs free energy changes (ΔG) for elementary reaction steps were calculated using the relation: $G = E_{\text{elec}} + E_{\text{ZPE}} - TS$, where E_{elec} is the DFT-calculated electronic energy at 0 K, E_{ZPE} is the zero-point energy, T is the temperature (set to 298.15 K), and S is the entropy.

To properly account for the strong electron correlation effects of transition metals, the GGA + U method was employed in both structural optimization and electronic structure calculations. The effective U (U_{eff}) values were set to 6.2 and 5.3 eV for Ni and Fe, respectively.

3.3 Results and Discussion

3.3.1 Synthesis and Characterization of M-NiFe and B,M-NiFe LDH

Composition-dependent Morphology and Phase Evolution in $\text{Al}_x\text{-NiFe}$ LDH

First, Al-doped NiFe LDH catalysts with varying Al content were synthesized via a one-step hydrothermal reaction ($\text{Al}_x\text{-NiFe}$ LDH, [Figure 3.1](#)). The incorporation of Al was controlled by adding 0, 0.07, 0.14, 0.28, and 0.56 mmol of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, respectively, which influenced the resulting morphology and structure of the LDH ([Figure 3.2](#)). As displayed in [Figure 3.2c, d](#), SEM images reveal that for lower Al content (*i.e.*, $x \leq 0.25$), the Al_x -doped LDH catalysts retain a nanosheet morphology that is vertically aligned and uniformly distributed across the NF substrate, similar to the undoped NiFe LDH ([Figure 3.2b](#)). However, at higher Al concentrations ($\text{Al}_{0.5}\text{-NiFe}$ and $\text{Al}_1\text{-NiFe}$ LDH), the morphology evolves into more densely packed nanostructures, transitioning from needle-like formations to flower-like nanocrystals ([Figure 3.2e, f](#)).

The structure of the catalysts was analyzed by XRD, confirming the presence of the characteristic LDH phase in the NiFe LDH, as well as in the $\text{Al}_{0.125}\text{-NiFe}$ LDH nanosheet samples ([Figure 3.3a](#)). In contrast, the $\text{Al}_1\text{-NiFe}$ LDH nanosheets exhibited additional

diffraction peaks around 31.3° , indicative of Al_2O_3 impurities, although the main diffraction pattern belonged to LDH.

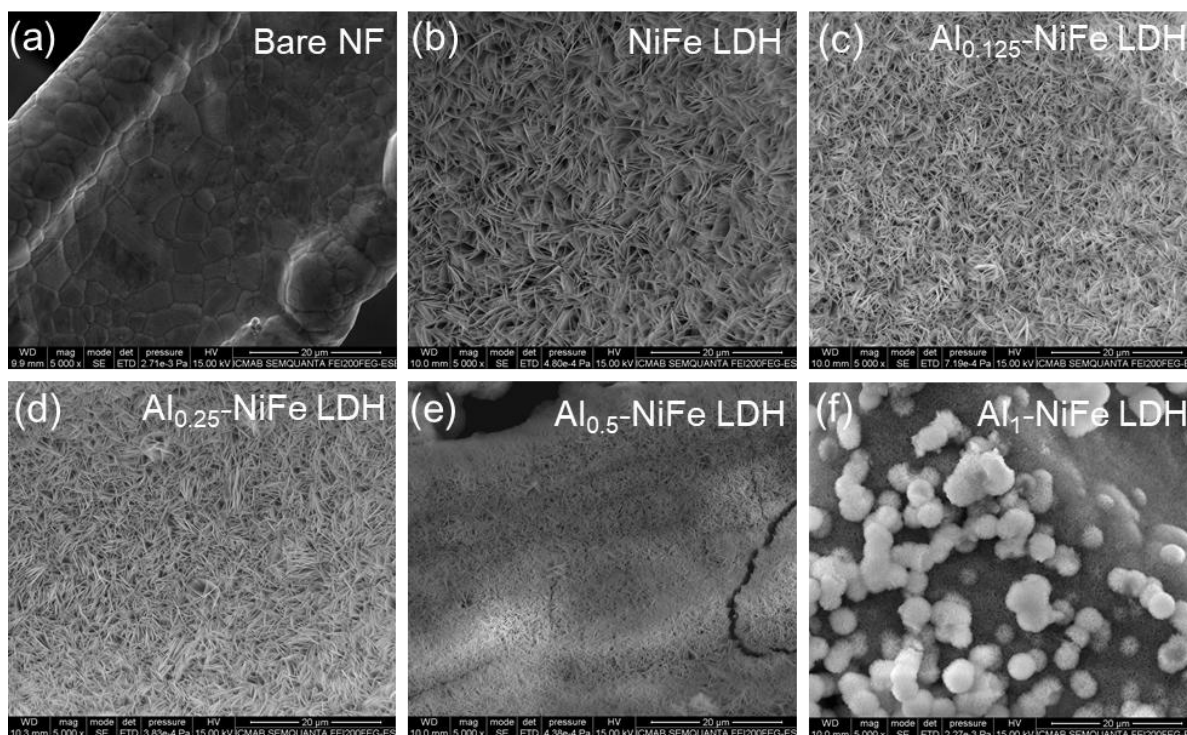


Figure 3.2 SEM images of (a) bare NF, (b) NiFe LDH, (c) $\text{Al}_{0.125}$ -NiFe LDH (Al-NiFe LDH), (d) $\text{Al}_{0.25}$ -NiFe LDH, (e) $\text{Al}_{0.5}$ -NiFe LDH, (f) Al_1 -NiFe LDH.

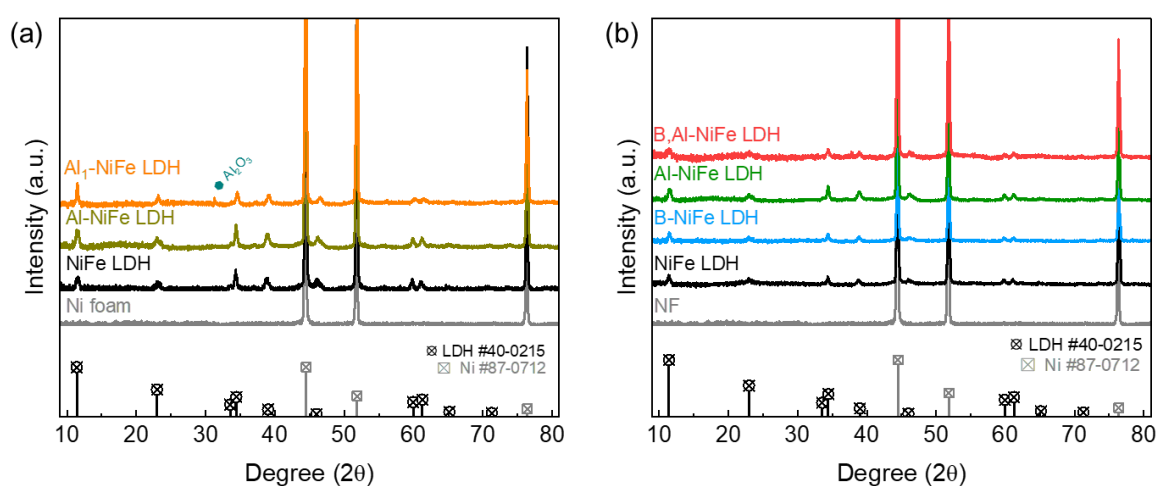


Figure 3.3 (a) The XRD patterns of NF, NiFe LDH, $\text{Al}_{0.125}$ -NiFe LDH (Al-NiFe LDH), and Al_1 -NiFe LDH. (b) The XRD patterns of B-NiFe LDH, $\text{Al}_{0.125}$ -NiFe LDH (Al-NiFe LDH), and B,Al-NiFe LDH.

The different Al_x -doped NiFe LDH nanosheets were then evaluated for the OER,

revealing that the best performance was achieved with the sample containing the lowest Al content ($x = 0.125$, [Figure 3.4a](#), red line). This observation is consistent with the trend reported by Yong-Tae Kim et al., where a 5% Al content in NiFe alloy results in an increase in the electrocatalytic performance.³⁹ Notably, at high Al content ($x = 1$), the catalytic performance dropped even below that of the undoped NiFe LDH control sample. These results support the conclusion that excessive Al doping (e.g., $\text{Al}_{0.5}$ -NiFe and Al_1 -NiFe LDH) induces a morphological transformation combined with the precipitation of secondary Al_2O_3 phases, which decrease the electrocatalytic performance.

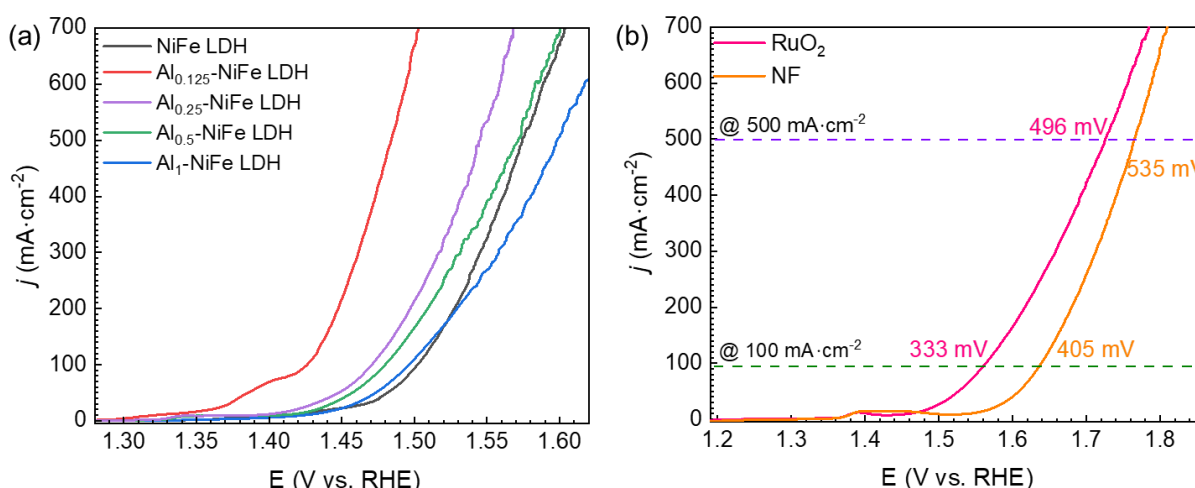


Figure 3.4 (a) The LSV curves of a series of Al_x -NiFe LDH in 1 M KOH, (b) LSV of NF and commercial RuO_2 in 1 M KOH

Synergistic Effects of B and Al doping on NiFe LDH

After identifying the $\text{Al}_{0.125}$ -NiFe LDH composition (hereafter Al-NiFe LDH) as the most active among Al-doped samples, boron was further incorporated into both NiFe and Al-NiFe LDH samples, resulting in a set of four samples: NiFe, B-NiFe, Al-NiFe, and B,Al-NiFe LDH ([Figure 3.2b, c](#), and [3.5](#)). Noteworthy, boron incorporation preserves the nanosheet structure, retaining its morphological advantages as well as the LDH structure, as confirmed by XRD characterization ([Figure 3.3b](#)).

The electrocatalytic performance for the OER in alkaline media was systematically evaluated in 1 M KOH (pH=14) using LSV. As shown in [Figure 3.6a](#), both B and Al doping significantly reduced the OER overpotentials compared to NiFe LDH. Specifically, the overpotentials at $100 \text{ mA}\cdot\text{cm}^{-2}$ decreased from 272 mV for NiFe LDH to 215 and 224 mV for B- and Al-doped NiFe LDH, respectively ([Figure 3.6b](#), [Table 3.1](#)). The slightly superior performance of B-NiFe LDH may be attributed to the higher B content in B-NiFe LDH (7 %) compared to the 4% Al content in Al-NiFe-LDH, as determined by elemental analysis ([Figure 3.7](#)). For comparison, commercial RuO_2 supported on NF and bare NF were also tested ([Figure 3.4b](#)). As expected, RuO_2 exhibited overpotentials of 333 and 496 mV at current densities of 100, and 500 $\text{mA}\cdot\text{cm}^{-2}$, respectively, better than 405 and 535 mV for bare NF. However, the values are significantly higher than those of the doped NiFe LDH catalysts, further confirming the effectiveness of B and Al incorporation in enhancing OER performance.

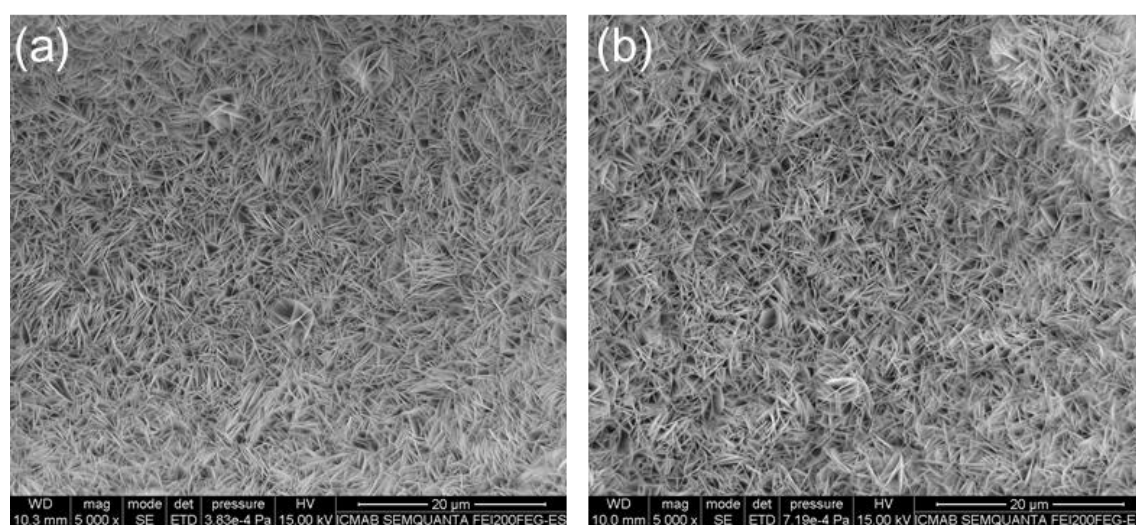


Figure 3.5 SEM images of (a) B-NiFe LDH, and (b) B,Al-NiFe LDH

Table 3.1 The summary of geometric overpotentials, Tafel slope, Cdl, ECSA, specific overpotential, and TOF of NiFe, B-NiFe, Al-NiFe, and B,Al-NiFe LDH.

		NiFe LDH	B-NiFe LDH	Al-NiFe LDH	B,Al-NiFe LDH
Geometric	$10 \text{ mA}\cdot\text{cm}^{-2}$	229	185	187	169
overpotential (mV)	$100 \text{ mA}\cdot\text{cm}^{-2}$	272	215	224	196

	500 mA·cm⁻²	344	279	287	254
Tafel slope (mV·dec⁻¹)		70.8	48.6	44.2	38.6
C_{dl} (mF·cm⁻²)		8.93	6.93	8.62	10.18
ECSA (cm²)		223.25	173.25	215.50	254.50
Specific overpotential (mV)	j_{ECSA}=1 mA·cm⁻²	337	260	279	255
TOF (s⁻¹)	1.50 V	0.27	1.89	1.30	2.05

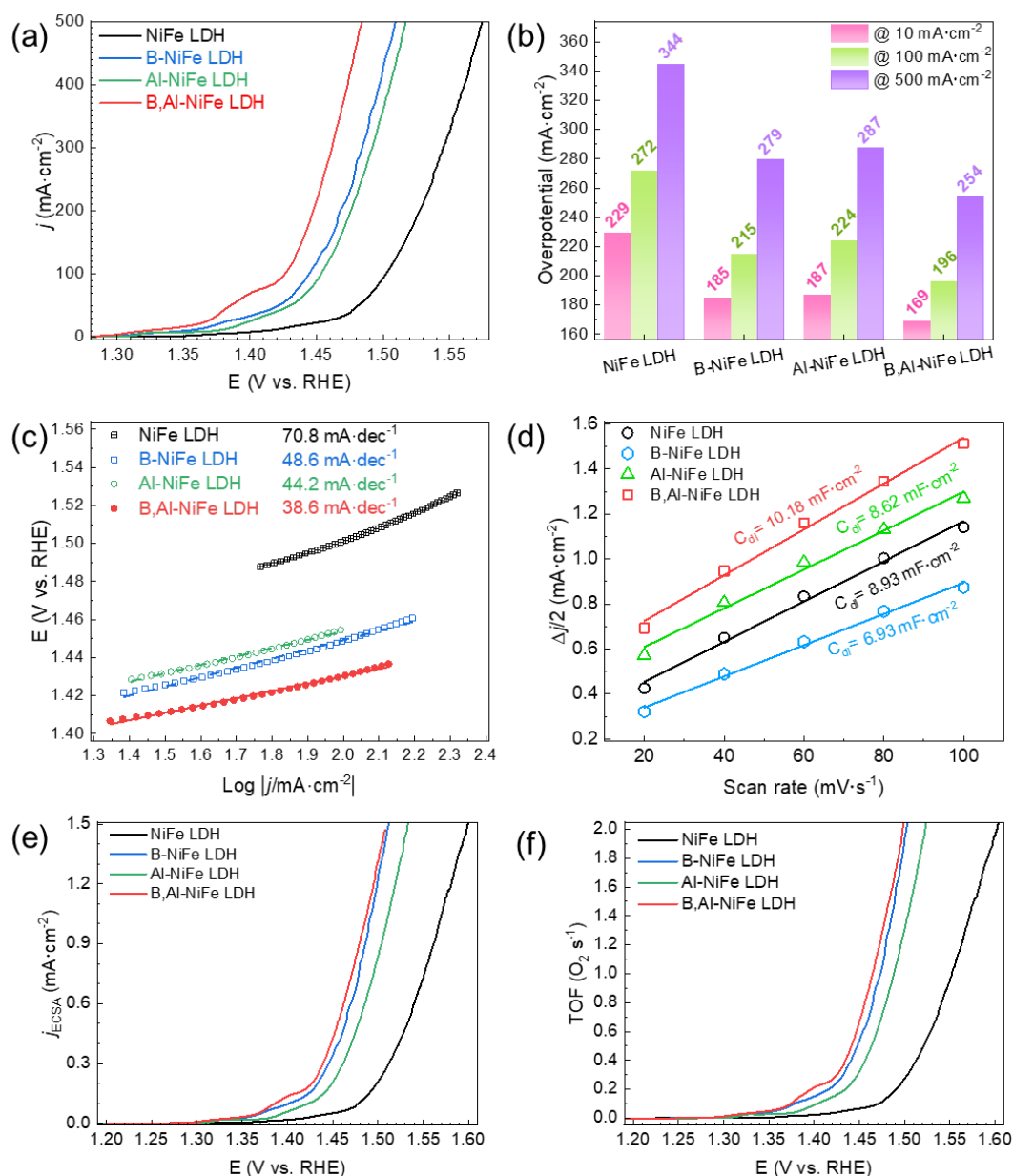


Figure 3.6 The electrocatalytic OER performance of NiFe, B-NiFe, Al-NiFe, and B,Al-NiFe LDH in 1.0 M KOH (pH=14): (a) LSV polarization curves, (b) the overpotentials at 10, 100, and 500 mA·cm⁻², (c) Tafel slopes, (d) C_{dl} calculation, (e) LSV curves normalized by ECSA, and (f) TOF calculations.

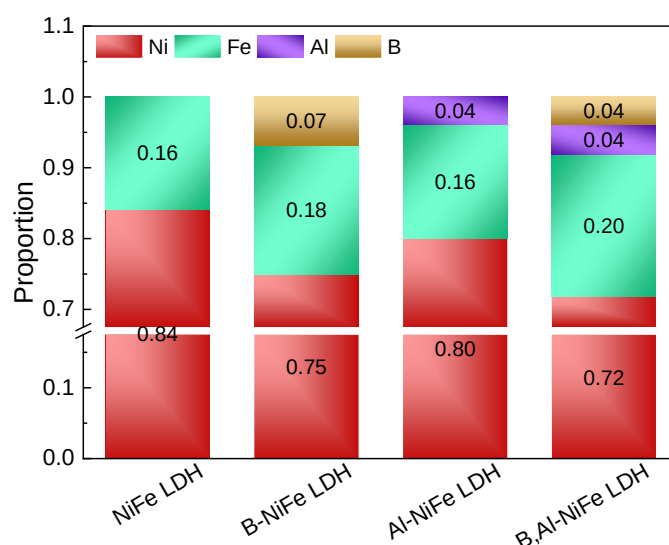


Figure 3.7 ICP-OES results to reveal the dopant loading.

Remarkably, the co-doping of B into Al-NiFe LDH resulted in a substantial enhancement in OER activity. The B,Al-NiFe LDH exhibited lower overpotentials of 169 and 196 mV at current densities of 10 and 100 $\text{mA}\cdot\text{cm}^{-2}$, respectively, compared to 185 and 215 mV for Al-NiFe LDH. At higher current densities, the performance gain became even more pronounced, for instance, B,Al-NiFe LDH showed an overpotential of 254 mV at 500 $\text{mA}\cdot\text{cm}^{-2}$, representing a 26% decrease compared to NiFe LDH (344 mV). Moreover, B,Al-NiFe LDH exhibited the lowest Tafel slope of all samples (38.6 $\text{mV}\cdot\text{dec}^{-1}$), indicating a superior OER kinetics and outperforming NiFe LDH (70.8 $\text{mV}\cdot\text{dec}^{-1}$), B-NiFe LDH (48.6 $\text{mV}\cdot\text{dec}^{-1}$), and Al-NiFe LDH (44.2 $\text{mV}\cdot\text{dec}^{-1}$) ([Figure 3.6c](#)).

Electrochemical double-layer capacitance (C_{dl}) values, derived from CV curves ([Figure 3.6a](#)), provided additional insight into surface activity. The B,Al-NiFe LDH exhibited the highest C_{dl} of 10.18 $\text{mF}\cdot\text{cm}^{-2}$, surpassing those of NiFe LDH (8.93 $\text{mF}\cdot\text{cm}^{-2}$), B-NiFe LDH (6.93 $\text{mF}\cdot\text{cm}^{-2}$), and Al-NiFe (8.62 $\text{mF}\cdot\text{cm}^{-2}$). Consistently, the ECSA calculations ([Table 3.1](#)) revealed the highest value for B,Al-NiFe LDH (254.50 cm^2), followed by NiFe LDH (223.25 cm^2), Al-NiFe LDH (215.50 cm^2), and B-NiFe LDH (173.25 cm^2).

While both B- and Al-doped samples exhibited improved OER activity, their reduced ECSA values suggest that some surface sites became less electrochemically accessible. This may be attributed to a shift in the reaction pathway, from the conventional AEM, dominant in pristine NiFe LDH, to the LOM, which alters surface reactivity and charge storage characteristics, the phenomenon is consistent with the observation in publication.⁴⁰ Remarkably, B,Al co-doping appears to alleviate this trade-off. The elevated ECSA suggests a synergistic effect, where B and Al together increase the proportion of LOM-active sites while simultaneously possibly modulating the electronic environment (e.g., via B-Al bonding) to facilitate AEM as well. This dual enhancement likely enables both mechanisms to coexist efficiently, thus maximizing the number of catalytically active sites.

Benchmarking and Long-term Stability of B,Al-NiFe LDH Catalyst

To evaluate the intrinsic activity of the catalysts, overpotentials were normalized considering the ECSA, as shown in [Figure 3.6e](#) and [Table 3.1](#). The B,Al-NiFe LDH sample presented the lowest intrinsic overpotential of 255 mV at an ECSA-normalized current density (j_{ECSA}) of $1.0 \text{ mA} \cdot \text{cm}^{-2}$, compared to 337, 260, and 279 mV for NiFe, B-NiFe, and Al-NiFe LDH, respectively. These results confirm that B,Al co-doping not only enhances apparent OER activity but also improves intrinsic site activity. A similar trend was observed for the TOF ([Figure 3.6f](#)) where B,Al-NiFe LDH achieved the highest TOF of 2.05 s^{-1} at 1.50 V vs. RHE, significantly outperforming NiFe (0.27 s^{-1}), B-NiFe LDH (1.89 s^{-1}), and Al-NiFe LDH (1.30 s^{-1}). Moreover, EIS revealed a low charge transfer resistance ($R_{\text{ct}} = 0.16 \Omega$), indicating fast interfacial charge transfer.

Given the excellent performance of the B,Al-NiFe LDH, we compared this sample with state-of-the-art LDH-based and derived catalysts, including CoFeAl LDH,⁴¹ NiFeMo(OH)₂,¹⁹ VB-FeNiP,¹⁸ and Ni₃S₂/Fe-NiP_x/NF,⁴² among others ([Figure 3.8b](#), listed in [Table 3.3](#)). Remarkably, B,Al-NiFe LDH achieves a favorable combination of

low overpotential and small Tafel slope, placing it among the most efficient LDH-type OER catalysts to date, particularly relevant for practical water splitting systems. Moreover, a stability test was carried out at a constant current density of $100 \text{ mA} \cdot \text{cm}^{-2}$ for 360 hours, confirming a negligible increase of only 1.4% in the applied voltage (from 1.43 to 1.45 V, [Figure 3.8c](#)). This remarkable stability is attributed to the self-sacrificial role of Al, which gradually dissolves to form $\text{Al}(\text{OH})_x$ species during OER, thereby stabilizing the catalyst.²²

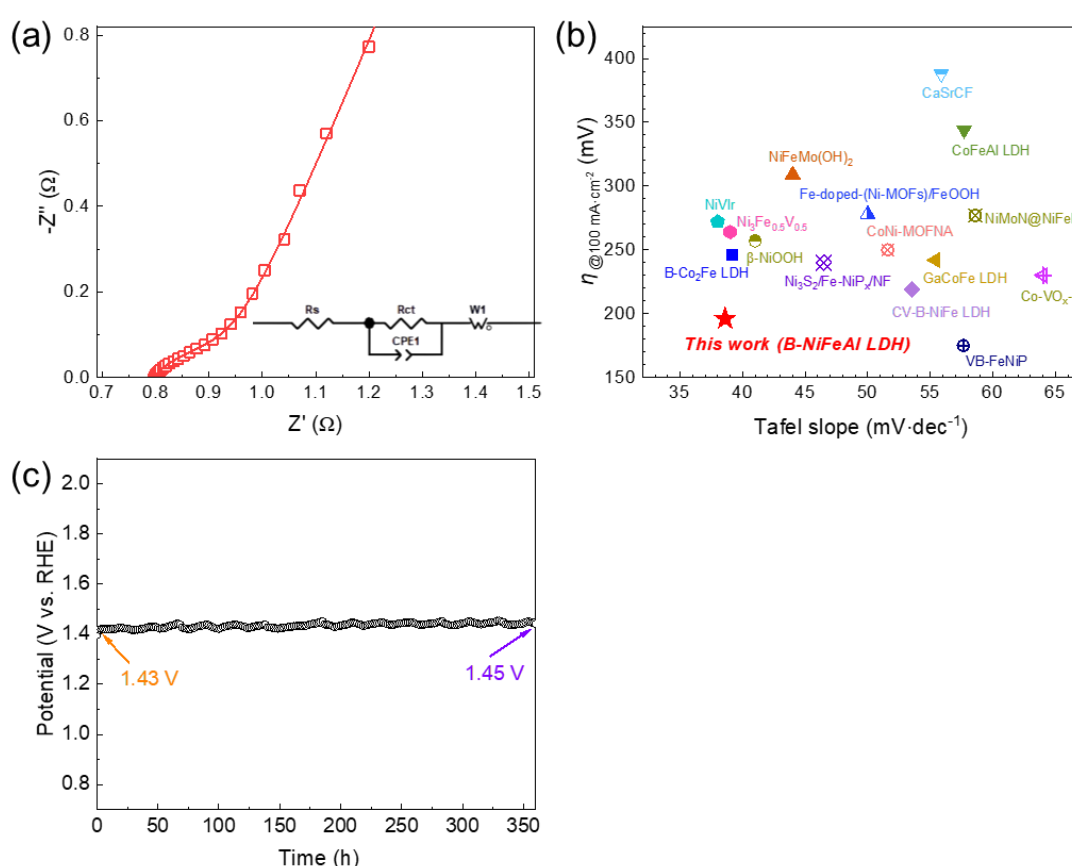


Figure 3.8 (a) EIS spectrum of B₂Al-NiFe LDH ([Table 3.2](#)), (b) comparison of B₂Al-NiFe LDH, and other related reported catalysts (listed in [Table 3.3](#)), (c) the CP curve of B₂Al-NiFe LDH is over 360 hours at current density of $100 \text{ mA} \cdot \text{cm}^{-2}$.

Table 3.2 The equivalent circuit data of B₂Al-NiFe LDH in [Figure 3.8a](#).

R_s (Ω)	R_{ct} (Ω)	CPE-T ($\text{mF} \cdot \text{cm}^{-2}$)	CPE-P ($\text{mF} \cdot \text{cm}^{-2}$)	W-R	W-T	W-P
0.80	0.16	0.17	0.61	$3.3\text{E-}5$	$5.2\text{E-}7$	0.40

Table 3.3 The comparison among as-synthesized B,Al-NiFe LDH with the state-of-the-art in freshwater.

Sample	Overpotential (mV) @ 100 mA·cm ⁻²	Tafel slope (mV·dec ⁻¹)	References
B,Al-NiFe LDH	196	38.6	This work
VB-FeNiP	175	57.64	18
NiFeMo(OH) ₂	309	44	19
CoFeAl-T-NaOH	344	57.7	43
CV-B-NiFe LDH	219	53.5	44
CaSrCF	388	55.87	45
GaCoFe LDH	242	55.4	41
B-Co ₂ Fe LDH	246	39.2	23
Ni ₃ S ₂ /Fe-NiP _x /NF	240	46.5	42
Fe-doped-(Ni-MOFs)/FeOOH	278	50	46
β-NiOOH	257	41	47
Ni ₃ Fe _{0.5} V _{0.5}	264	39	48
Co-Vo _x -P	230	64	49
NiVlr-LDH	272	38	50
CoNi-MOFNA	250	51.6	51
NiMoN@NiFeN	277	58.6	52

3.3.2 Structural and surface analysis for B,Al-NiFe LDH

Atomic distribution and crystalline structure

To examine the atomic distribution in B,Al-NiFe LDH, HAADF-STEM image and the corresponding elemental mapping were performed ([Figure 3.9b](#)), confirming a uniform distribution of Ni, Fe, Al, O, and B across the nanosheets. The precise elemental ratio was evaluated by ICP-OES, indicating 72% of Ni, 20% of Fe, and 4% of each of B and Al ([Figure 3.7](#)), which is consistent with the targeted doping levels (see experimental section).

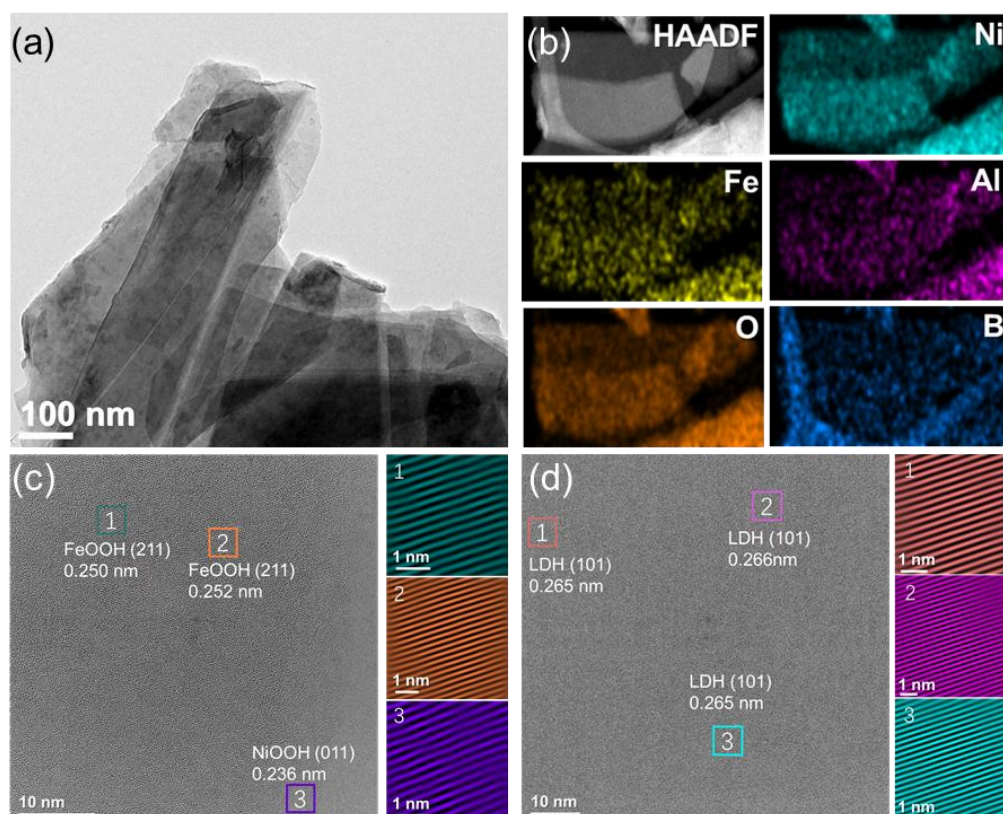


Figure 3.9 Characterization of B₃Al-NiFe LDH: (a) TEM image, (b) HAADF-EDX elemental mapping, and (c, d) HR-TEM images and fast Fourier transform (FFT) patterns of B₃Al-NiFe LDH with lattice spaces on the edge and in the center of the nanosheet, respectively.

In addition, HR-TEM images revealed distinct lattice fringes of 0.250 and 0.236 nm, corresponding to the (211) plane of FeOOH and the (011) planes of NiOOH, respectively ([Figure 3.9c](#)). This confirms the presence of highly active *OOH species on the surface, which are widely considered as the promoted intermediates for boosting OER. Besides the appearance of *OOH, several lattice spacings of ~0.265 nm were distinguished in [Figure 3.9d](#), revealing the LDH phases (101).

Surface States and Coordination Environment

The surface composition and coordination environment of B₃Al-NiFe LDH were analyzed by XPS spectra ([Figure 3.10](#)). The Ni 2p spectrum ([Figure 3.10b](#)) displays spin-orbit doublets at 876.00 (Ni 2p_{1/2}) and 858.60 eV (Ni 2p_{3/2}), further deconvoluted into 10 peaks corresponding to 4 satellites (882.36, 879.42, 864.46, and 861.86 eV),

Ni^{3+} (876.00, and 858.30 eV), Ni^{2+} (873.79, and 854.82 eV), and two peaks that can be assessed to a Ni-B bond (872.14, and 852.56 eV).⁵³ On the one hand, the $\text{Ni}^{3+}/\text{Ni}^{2+}$ ratio (2.29) suggests a higher content of Ni^{3+} species, which are beneficial for OER.^{54,55} On the other hand, Ni-B bonds constitute $\sim 2.9\%$ of the signal, evidencing B coordination with Ni. Similarly, the Fe 2p spectrum ([Figure 3.10c](#)) can be deconvoluted into 2 satellites (733.44, and 720.22 eV), Fe^{3+} (728.57, and 715.09 eV), Fe^{2+} (726.28, and 710.96 eV), and Fe-B (724.17, and 707.68 eV),⁵³ with a $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio of 1.82. Notably, Fe-B bonds represent a $\sim 11.8\%$, indicating a stronger tendency of Fe atoms to form stable B coordination compared to Ni. The Al 2p spectrum ([Figure 3.10e](#)) confirms the presence of 3 different peaks attributed to AlOOH (75.92 eV), Al-O (73.97 eV), and Al-B (70.51 eV) species. Noteworthy, Al-B was the dominant component (78.4%), underscoring the role of B doping in modulating local coordination and electronic structure in Al-NiFe LDH.

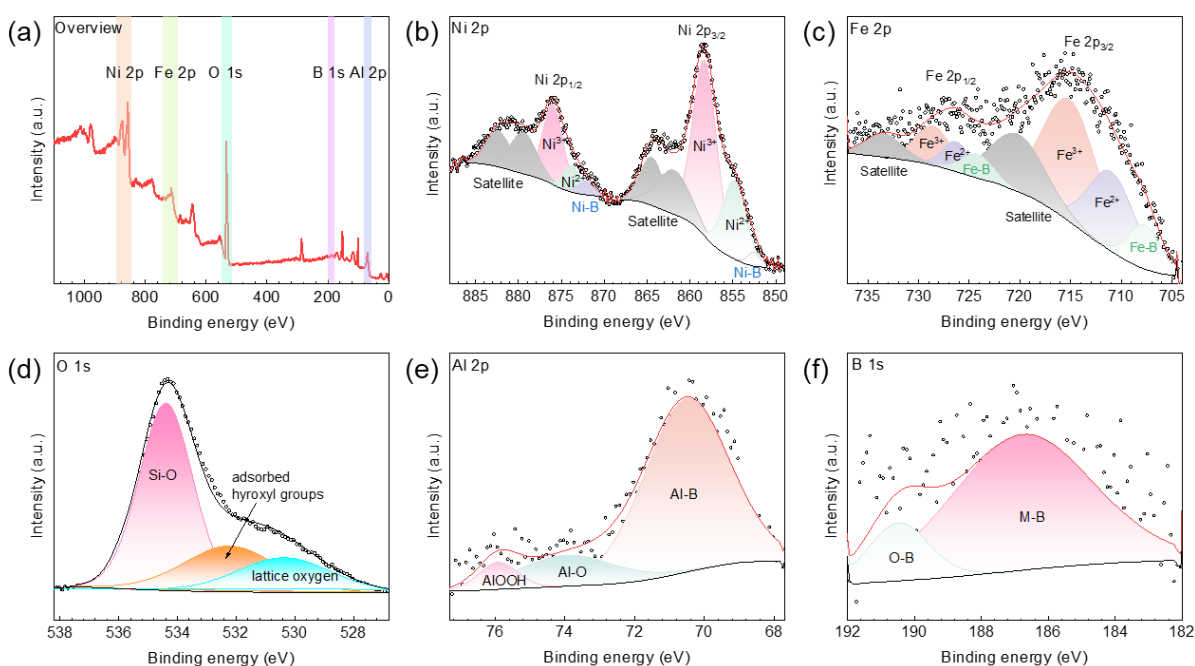


Figure 3.10 XPS investigation of B,Al-NiFe LDH and NiFe LDH, (a) overview, (b) Ni 2p, (c) Fe 2p, (d) O 1s, (e) Al 2p, and (f) B 1s.

The O 1s spectrum ([Figure 3.10d](#)) was deconvoluted into three components at 534.39,

532.22, and 530.36 eV. The highest binding energy contribution at 534.39 eV is attributed to the native SiO₂ layer of the Si water substrate and/or minor adventitious carbonate species. The 532.22 eV peak corresponds to surface hydroxyl groups preferentially adsorbed at defect sites, which are commonly associated with oxygen vacancy (O_v) related surface defects.⁵⁶ Although XPS cannot directly probe O_v, the enhanced intensity of this hydroxyl component (ca. 24%) is widely considered as indirect evidence of vacancy-related sites, in line with recent discussions on O 1s peak assignments in oxides.^{57–62} Finally, the peak at ~530.36 eV is assigned to lattice oxygen (M-O) in the LDH framework. The relatively high fraction of the 532.22 eV contribution is consistent with the NaBH₄ reduction procedure, which partially removes lattice oxygen, generates defect sites, and thereby facilitates charge transport and the adsorption/activation of oxygenated intermediates. During this process, the strong reducing environment leads to the partial removal of lattice oxygen, thereby generating O_v. The B 1s spectrum ([Figure 3.10f](#)) confirms metal-B bond formation at 186.77 eV,⁵³ indicating successful incorporation of boron species into the LDH structure. While boron doping may affect the local electronic environment, a direct correlation between B insertion and O_v formation requires further evidence.

Surface Wettability and Interfacial Properties

Surface properties also play a key role in catalytic performance, accordingly, surface wettability was evaluated via contact angle measurements.^{63,64} As shown in [Figure 3.11a](#), bare NF exhibits a hydrophobic character with a water contact angle of 119°, limiting electrolyte infiltration. In contrast, when the NF are coated with NiFe LDH, the hydrophilicity is dramatically increased with water droplets spreading instantaneously (< 0.1 s) and being rapidly absorbed ([Figure 3.11b](#)). The same improvement was observed for B-NiFe, Al-NiFe, and B,Al-NiFe LDH samples in [Figure 3.11c-e](#), highlighting the formation of a hydrophilic surface that facilitates efficient electrolyte diffusion, thus improving catalytic efficiency.

The above discussion suggests that B atoms are successfully incorporated into the LDH lattice, forming bonds with Al, Fe, and Ni, while concurrently inducing abundant O_v . This dual modulation alters the local charge density around the Ni and Fe active sites, enhancing LOM pathways. Additionally, the superhydrophilic surface promotes efficient electrolyte diffusion. The synergistic interplay between M-B bonding, O_v generation, and favorable interfacial properties boosts the overall OER electrocatalytic activity of B,Al-NiFe LDH beyond the state-of-the-art for LDH-based electrocatalyst for OER.

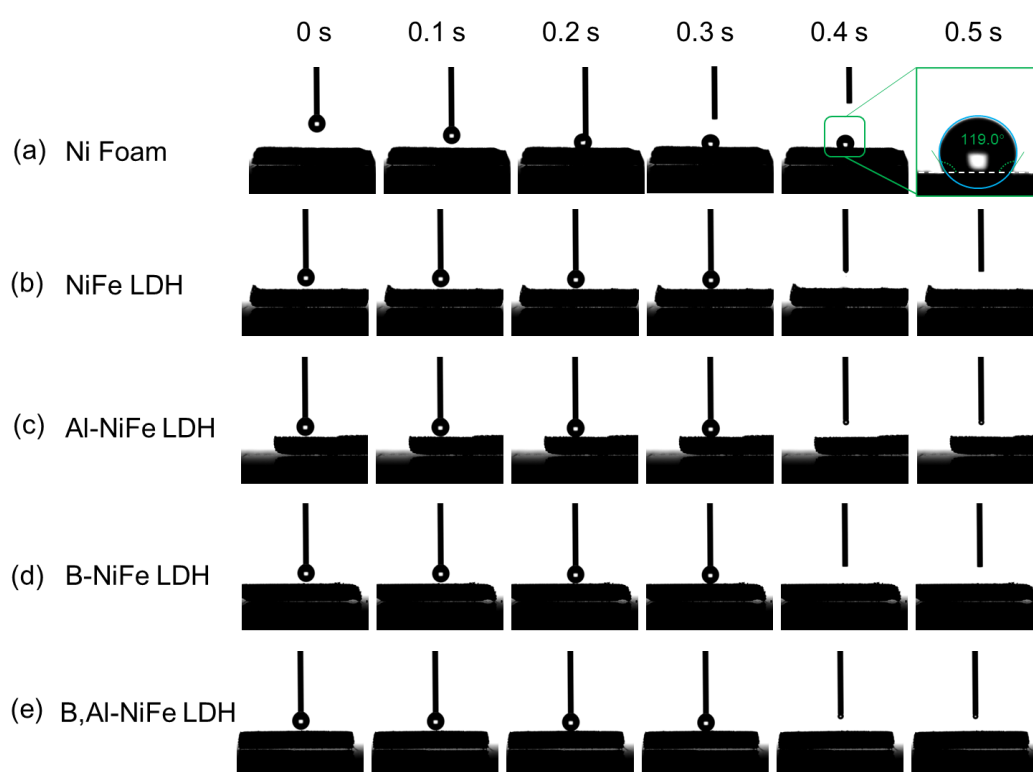


Figure 3.11 Real-time contact angle images shot of (a) NF, (b) NiFe LDH, (c) Al-NiFe LDH, (d) B-NiFe LDH, and (e) B,Al-NiFe LDH

Replacing Al by Ga and In in M-NiFe LDH

To further explore the role of doping NiFe LDH, Ga- and In-NiFe LDH nanosheets were grown on top of NF using the same synthesis protocol, but replacing the Al salt with Ga and In ones (see experimental session). Note that Ga and In belong to the same group as Al in the periodic table, hence sharing similar valence electron configurations

and coordination chemistries. Structural characterization revealed that Ga- or In-NiFe LDH showed a denser structure compared to Al-NiFe LDH according to the SEM images ([Figure 3.12](#)). LSV measurements confirmed that the overpotentials for Ga- and In-NiFe LDH were still lower than NiFe LDH ([Figure 3.13a](#)). Interestingly, the catalytic performance seems to be inversely correlated with ionic radii of the dopants ($r_B = 0.27 \text{ \AA}$, $r_{Al} = 0.53 \text{ \AA}$, $r_{Ga} = 0.62 \text{ \AA}$, and $r_{In} = 0.80 \text{ \AA}$), suggesting a potential relationship between catalytic performance and ionic size. Smaller dopant ionic radii, such as those of B and Al, may integrate more effectively into the LDH lattice, enhancing electronic modulation and catalytic activity with minor lattice distortion.

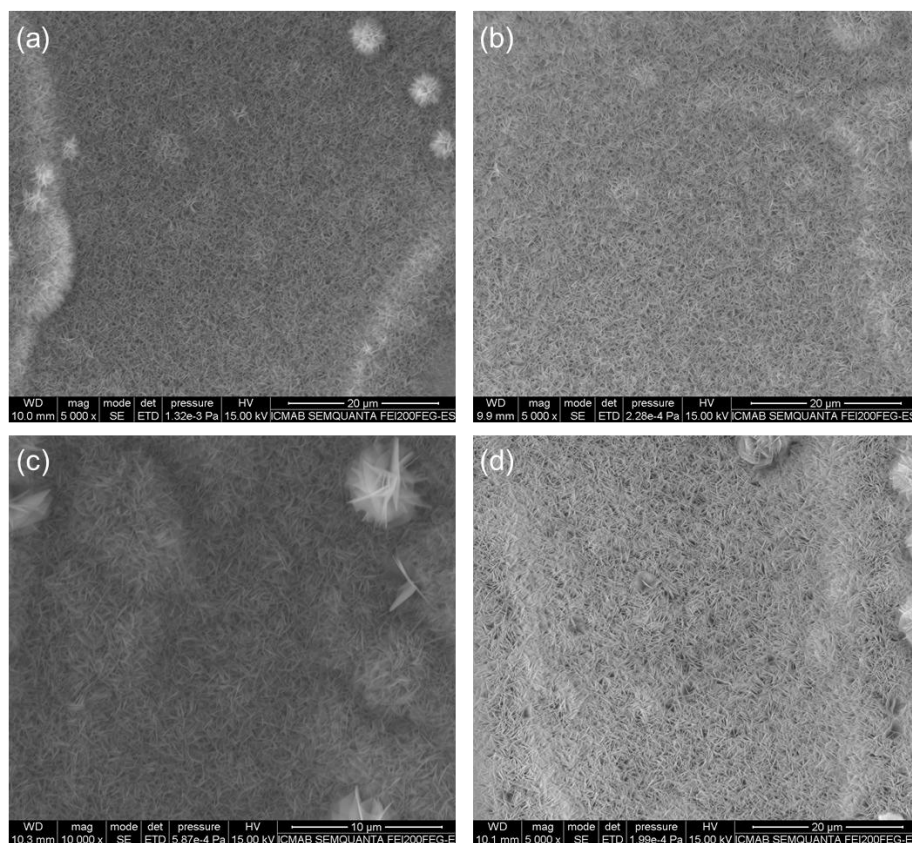


Figure 3.12 The SEM images of (a) Ga-NiFe LDH, (b) B,Ga-NiFe LDH, (c) In-NiFe LDH, and (d) B,In-NiFe LDH

As previously discussed for Al-NiFe LDH, B was introduced into Ga- and In-NiFe LDH, leading to an improvement of the electrocatalytic activity compared to their respective

mono-doped counterparts ([Figure 3.13c](#), [3.14](#)). This result reinforces the hypothesis that B plays a pivotal role in enhancing catalytic efficiency. Similar to B,Al-NiFe-LDH, XPS analysis was conducted on both samples ([Figure 3.15](#)). Noteworthy, no detectable B 1s signal was observed for both Ga- and In-NiFe LDH. Moreover, neither In nor B signals were clearly observed in the XPS spectrum of B,In-NiFe LDH. This may be attributed to the low doping concentration of the heteroatoms, possibly due to the larger ionic radius of In, which makes lattice incorporation more difficult. In contrast, the B content in B,Al-NiFe LDH was significantly higher than those in B,Ga-NiFe and B,In-NiFe LDH, suggesting that Al may facilitate the stabilization of B within the lattice, possibly through a favorable synergistic interaction.

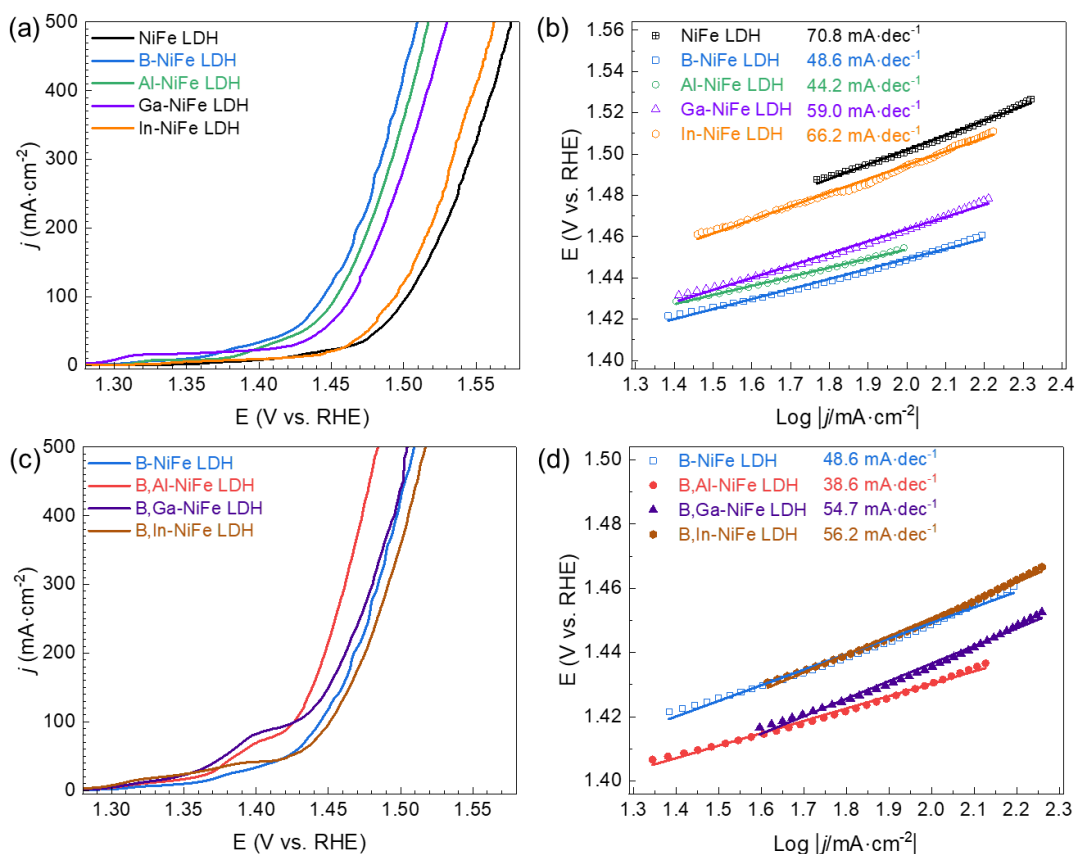


Figure 3.13 (a) LSV of single doped NiFe LDH by B, Al, Ga, and In, (b) the corresponding Tafel slopes of samples in [Figure 3.13.a](#), (c) LSV of dual doped NiFe LDH by B and Al, Ga, or In, (d) the corresponding Tafel slopes of samples in [Figure 3.13.c](#).

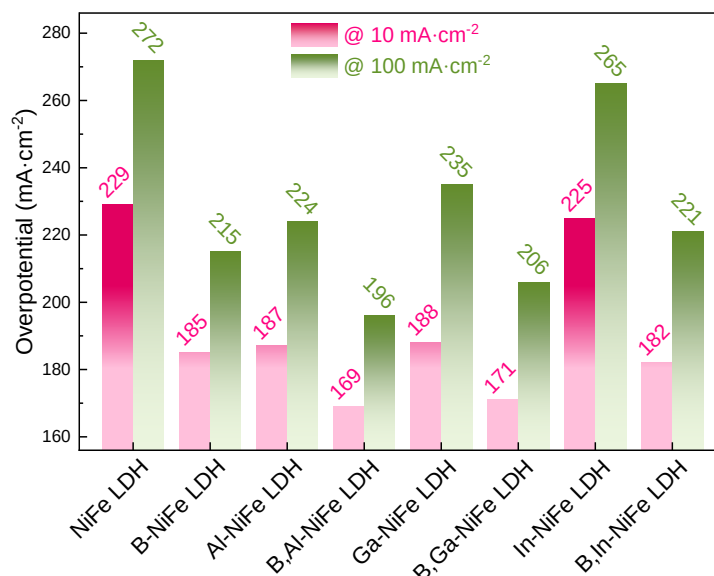


Figure 3.14 The summarized overpotentials at current densities of 10 and 100 mA·cm⁻² of as-synthesized samples.

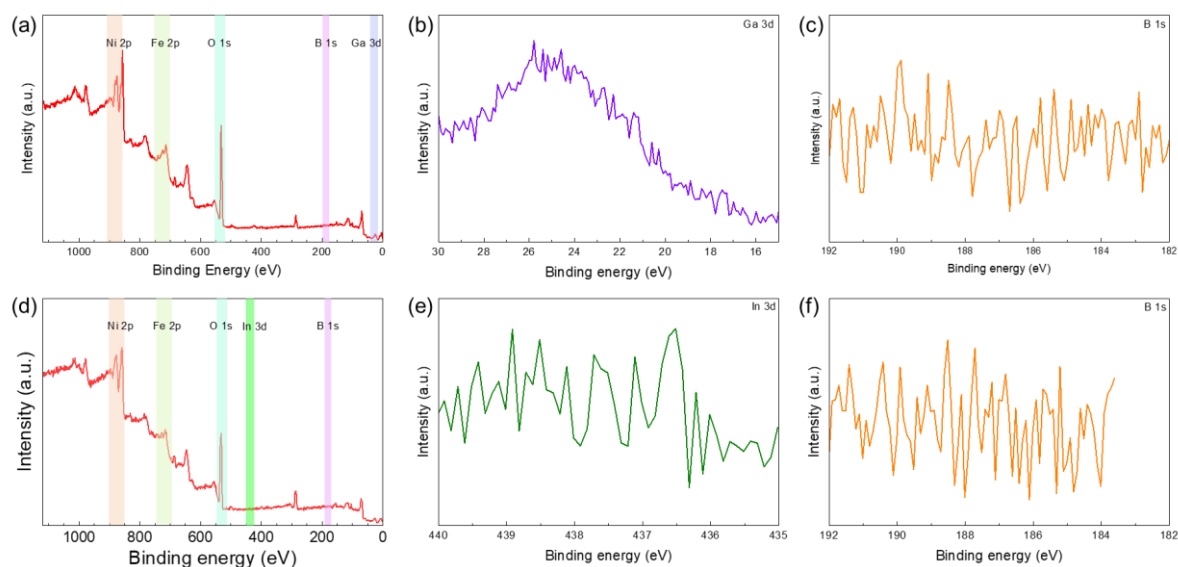


Figure 3.15 The XPS spectra of B,Ga-NiFe LDH (a) overview, (b) Ga 3d, (c) B 1s, and B,In-NiFe LDH (d) overview, (e) In 3d, (f) B 1s.

3.3.3 Electrocatalytic LOM Mechanism

To gain physical insights into how Al and B co-doping enhances the OER electrocatalytic performance of NiFe LDH, DFT simulations were conducted. Optimized atomic models for Al-NiFe LDH and B,Al-NiFe LDH single layers are

presented in [Figure 3.16a](#) and [3.16b](#), where Al atoms replace Ni atoms, and B atoms substitute the OH⁻ groups originally coordinated with Ni, Fe, and Al atoms, forming new M-B-M linkages that modulate the local electronic environment.

Charge density difference analysis ([Figure 3.16c](#)) clearly reveals pronounced electron redistribution upon B doping, where yellow and cyan regions represent electron accumulation and depletion, respectively.⁶⁵ Specifically, electron density markedly accumulates around B atoms, whereas neighboring Ni and Fe atoms exhibit electron depletion, indicating electron transfer from metal centers towards B and adjacent oxygen atoms. This observation is consistent with the high valence detected for the Fe and Ni by XPS, and supports the formation of M-B bonds in the LDH lattice. Rather than reinforcing M-O covalency, B doping substitutes bridging hydroxyl groups and induces strong local charge polarization, thereby modulating the coordination environment and electronic structure. This modification facilitates lattice oxygen activation and contributes to the enhanced OER kinetics.

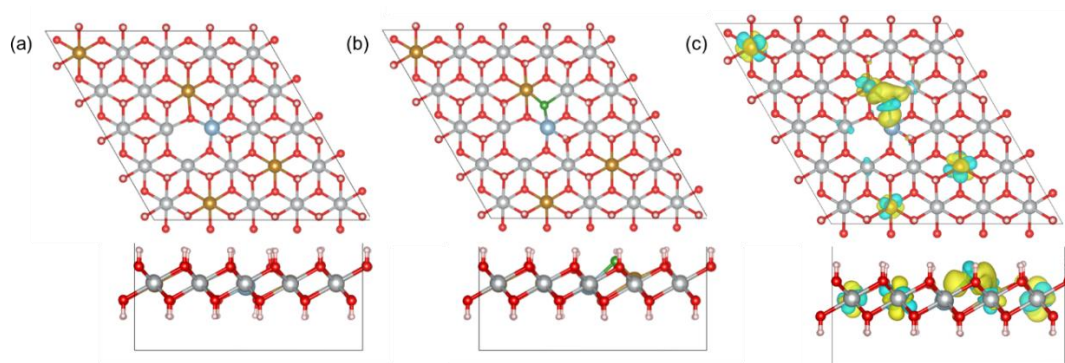


Figure 3.16 Geometric configurations of (a) Al-NiFe LDH and (b) B,Al-NiFe LDH (red atoms: oxygen, white atoms: hydrogen, grey atoms: nickel, brown atoms: iron, blue atoms: aluminum, green: boron). (c) Top and side views of differential charge diagram for B,Al-NiFe LDH (the yellow and cyan areas represent the electron accumulation and depletion, respectively).

Quantitative Bader charge analysis further characterizes this electron transfer, showing that B atoms carry approximately -1.00 e charge, while the charges of adjacent Al, Fe, and Ni atoms decrease from $+2.40$, $+1.39$, and $+1.26$ e to $+2.19$, $+1.29$, and $+1.12$ e,

respectively ([Table 3.4](#)).⁶⁶ This highlights a localized electronic modulation enhancing the catalytic activity of metal centers and potentially stabilizing oxygen intermediates during the reaction.

Table 3.4 Bader energies of Al-NiFe LDH and B,Al-NiFe LDH

	Bader energies (eV)			
	B	Al	Fe	Ni
Al-NiFe LDH	-	+2.40	+1.39	+1.26
B,Al-NiFe LDH	-1.00	+2.19	+1.29	+1.12

- No data

Electronic structure analysis based on total and projected density of states (TDOS and PDOS, [Figure 3.17a](#), and [3.17b](#)) provides further insight into the role of B doping in modulating the catalytic activity of Al-NiFe LDH. As shown in [Figure 3.17a](#), TDOS calculations reveal significant orbital overlap among Ni, Fe, and O states, indicating strong M-O hybridization.⁶⁷ Upon B incorporation, the bandgap slightly increases from 0.15 to 0.26 eV. Interestingly, this change is accompanied by the appearance of localized electronic states near the Fermi level,⁶⁸ which may act as mid-gap states facilitating charge transport. These states can effectively lower the activation barrier for electron hopping, thereby improving the charge mobility and potentially accelerating electron transfer during OER. Further PDOS analysis shows that these newly formed states arise predominantly from B 2p orbitals, with contributions exceeding those from lattice O 2p orbitals in the same energy region. This highlights a stronger electronic perturbation introduced by B dopants compared to the native oxygen atoms. Moreover, the partial overlap of Ni 3d, Fe 3d, and B 2p orbitals confirms the formation of new M-B bonding interactions, which help tailor the local electronic environment and contribute to improved electrical conductivity and catalytic performance.

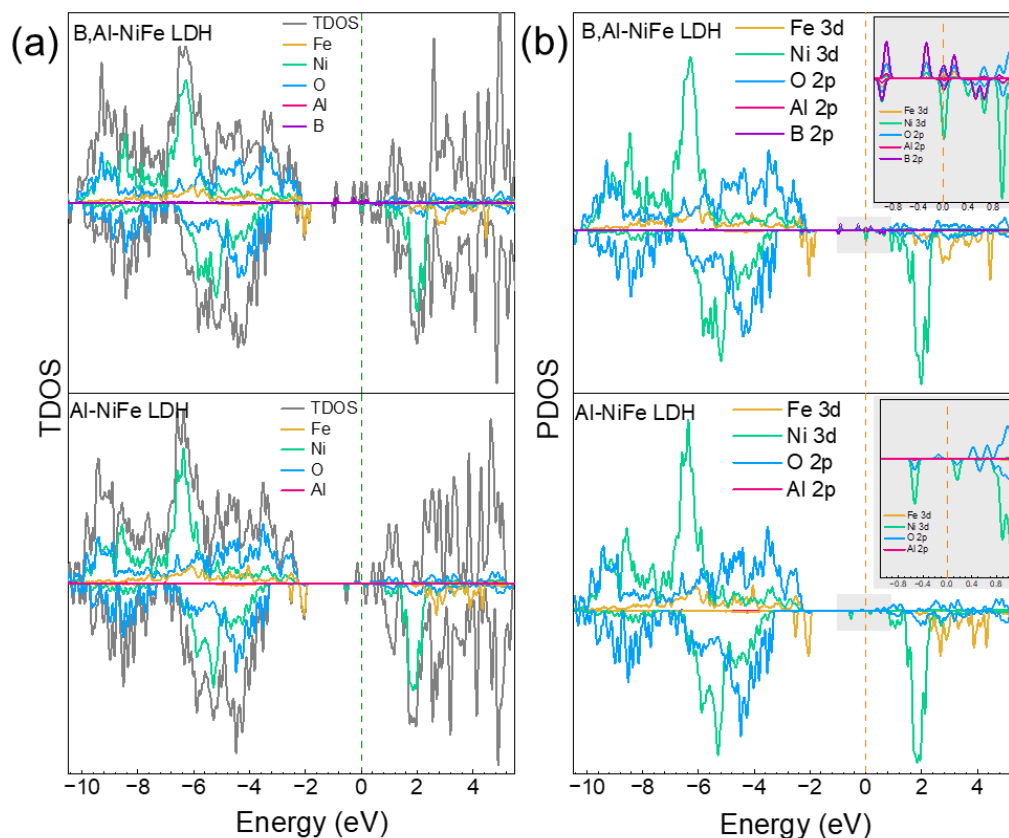


Figure 3.17 (a) Total density of states (TDOS) of Al-NiFe LDH and B,Al-NiFe LDH. (b) Projected density of states (PDOS) of Fe 3d, Ni 3d, O 2p, Al 2p, and B 2p.

The catalytic consequence of this electronic modulation is demonstrated by DFT-based free energy calculations for the OER process ([Figure 3.18](#), [3.19](#) and [3.20](#)).⁶⁹ The results reveal that lattice oxygen atoms are directly involved in the O-O bond formation step, supporting a LOM pathway. The rate-determining step (RDS), corresponding to the coupling of lattice oxygen with an adsorbed *O species, requires a free energy change of 3.15 eV in Al-NiFe LDH. With B doping, this value decreases to 2.80 eV, indicating a significant reduction in activation energy. Based on these values, the theoretical overpotential decreases from 192 to 157 mV, clearly demonstrating that B facilitates lattice oxygen activation and reduces the energy barrier for O-O bond formation.⁷⁰ This energetic improvement aligns with the earlier electronic structure and charge analysis, completing the mechanism that B and Al co-doping promotes the LOM pathway by simultaneously modulating the local coordination environment, inducing

charge polarization, and lowering the kinetic barrier, thus resulting in superior OER catalytic performance.

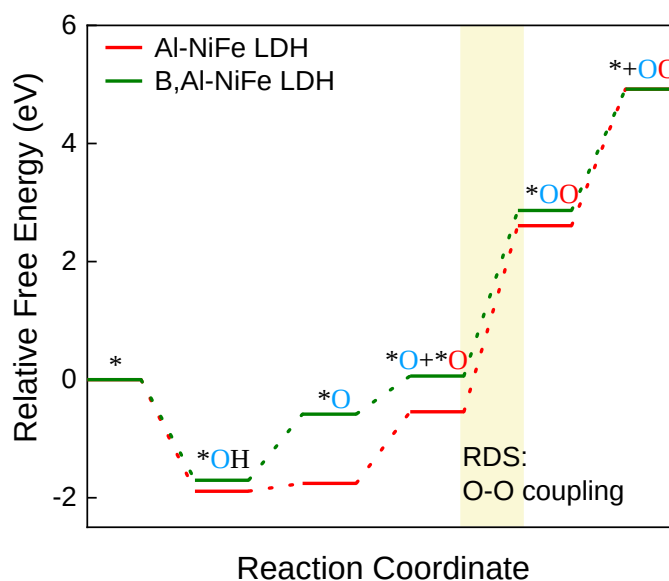


Figure 3.18 Gibbs energy diagrams of LOM pathway on Al-NiFe LDH and B,Al-NiFe LDH.

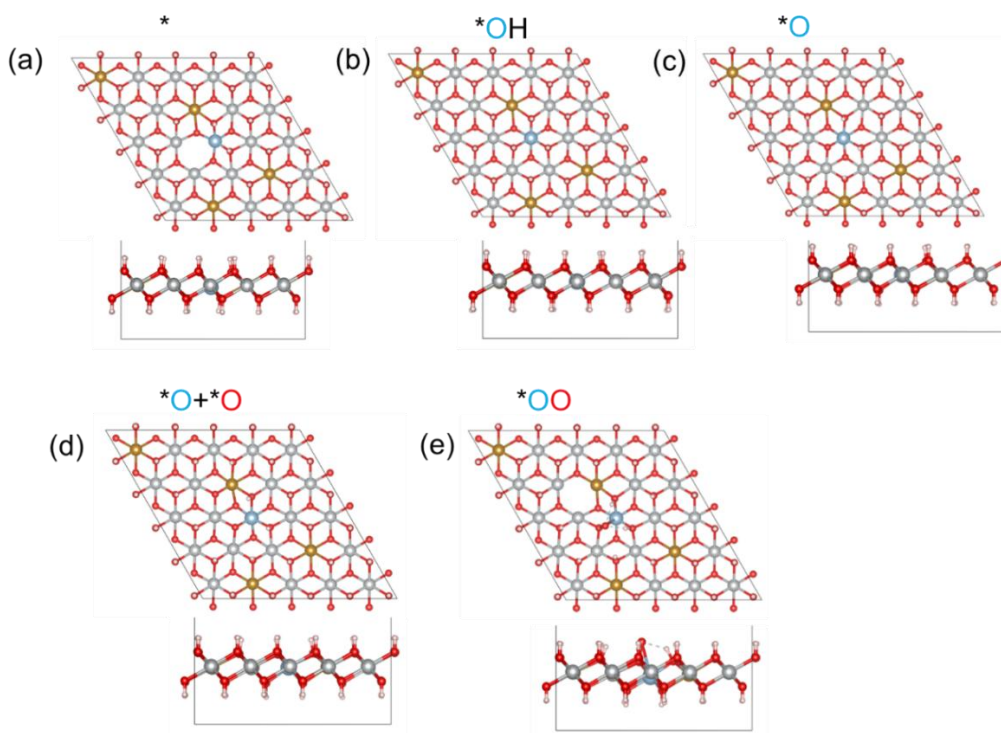


Figure 3.19 The geometric configurations and the intermediate adsorption on Al-NiFe LDH

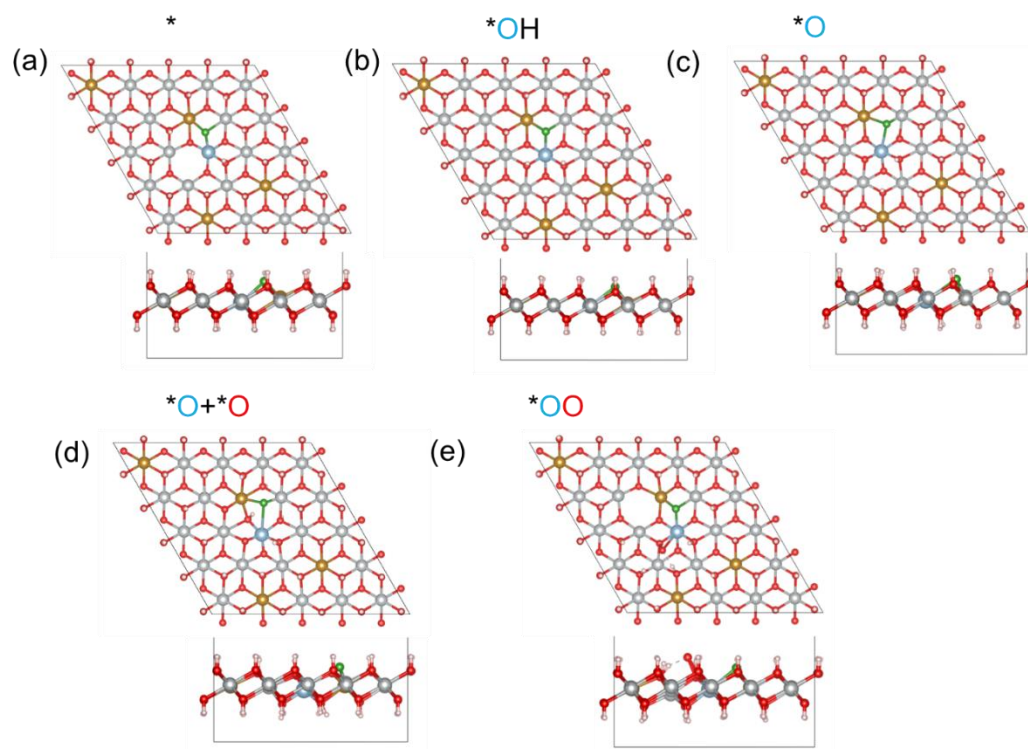


Figure 3.20 The geometric configurations and the intermediate adsorption on B,Al-NiFe LDH

To experimentally corroborate the LOM pathway predicted by DFT, pH-dependent OER measurements and chemical probe experiments were conducted.^{71,72} As shown in [Figure 3.21a](#), the current density of the B,Al-NiFe LDH catalyst increases with increasing pH, indicating that the reaction kinetics are dominated by chemical deprotonation steps characteristic of a non-concerted proton-electron transfer (non-CPET) pathway.^{21,73} This pH dependence suggests that the RDS is sensitive to OH⁻ concentration and likely involves lattice oxygen participation. Furthermore, tetramethylammonium (TMA⁺) was introduced as a selective chemical probe to distinguish between the LOM and AEM ([Figure 3.21b](#)). TMA⁺ is known to electrostatically interact with negatively charged peroxo-like (O₂²⁻) intermediates.^{74,75} Upon TMAOH addition, the OER activity of B,Al-NiFe LDH was significantly attenuated, and the Tafel slope increased from 38.6 to 82.8 mV·dec⁻¹ ([Figure 3.21c](#)), reflecting a notable suppression of lattice oxygen involvement.^{71,72,76}

These experimental observations, together with theoretical predictions, provide strong

evidence that B doping promotes the LOM pathway by enabling lattice oxygen activation, stabilizing reactive intermediates, and reducing the energy barrier for O-O bond formation. This dual validation confirms that B,Al co-doping is an effective strategy to enhance the intrinsic activity of NiFe LDH-based OER catalysts.

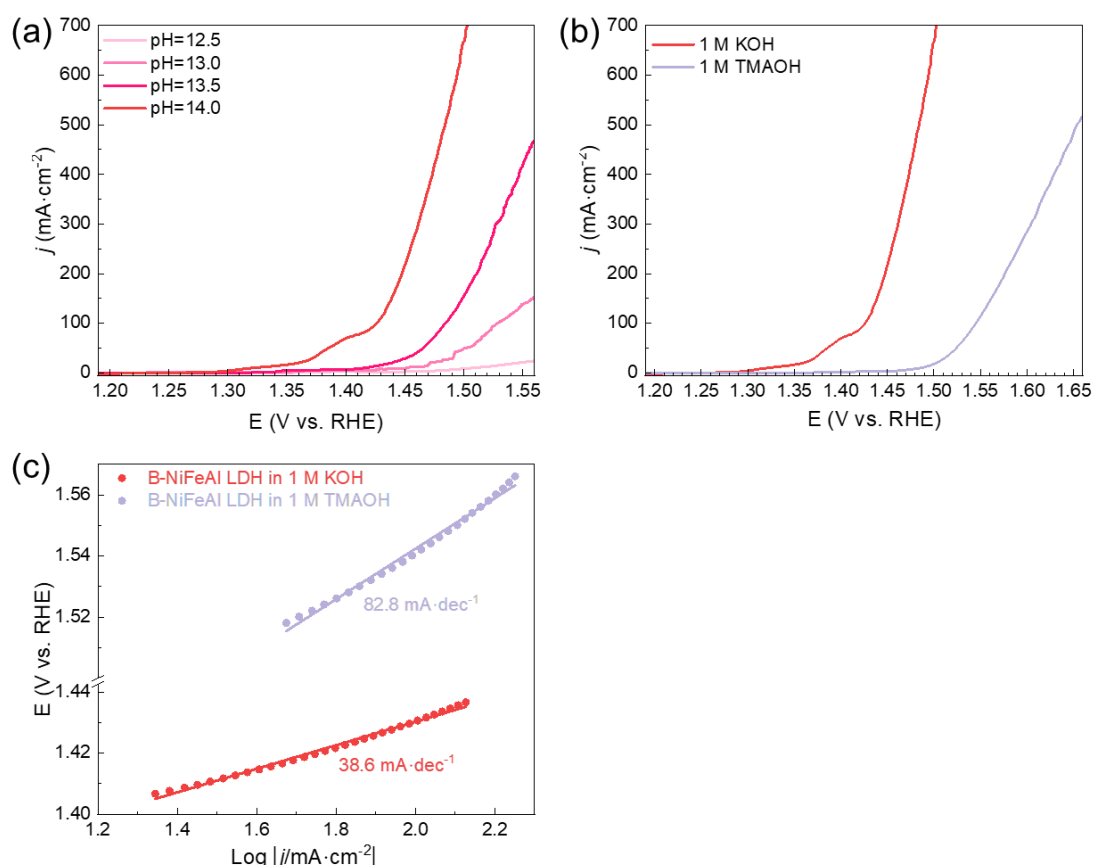


Figure 3.21 Experimental research on LOM evolution of B,Al-NiFe LDH for OER: (a) polarization curves of B,Al-NiFe LDH in alkaline electrolytes with different pH (12.5, 13.0, 13.5, and 14.0). (b) polarization curves in 1 M KOH and 1 M TMAOH, respectively. (c) The corresponding Tafel slopes of [Figure 3.21b](#).

3.3.4 Evaluation of OER Activity in Alkaline Natural Seawater

Direct seawater electrolysis presents a sustainable and promising solution for coastal and offshore energy systems, enabling scalable green hydrogen production. However, its practical implementation is hindered by challenges such as catalyst degradation, competing chloride oxidation, and scaling caused by divalent ions (e.g., Ca^{2+} and Mg^{2+}).

In this work, we evaluated the performance and stability of B,Al-NiFe LDH in natural seawater, using a 1 M KOH + seawater (Barceloneta Beach, Barcelona, Spain) electrolyte mixture.

The B,Al-NiFe LDH catalyst demonstrates excellent OER performance, delivering overpotentials of 250, 274, and 329 mV to achieve current densities of 100, 200, and 500 $\text{mA}\cdot\text{cm}^{-2}$, respectively ([Figure 3.22a](#)). Following this, we compared the overpotential at 100 $\text{mA}\cdot\text{cm}^{-2}$ with recently reported seawater OER electrocatalysts ([Figure 3.22b](#), [Table 3.5](#)). Remarkably, the B,Al-NiFe LDH achieves low overpotential, surpassing the $\text{MnO}_2@\text{NiFe LDH/NF}$ (276 mV),⁷⁷ B,Fe-CoP/NF (282 mV),²⁵ $\text{Ni}_3\text{S}_2/\text{Fe-NiP}_x$ (290 mV),⁴² et al. A Tafel slope ([Figure 3.22c](#)) of $43.1 \text{ mV}\cdot\text{dec}^{-1}$ further confirms the favorable reaction kinetics. Most notably, the catalyst retains over 98.5% of its initial activity after 360 hours of continuous operation at 100 $\text{mA}\cdot\text{cm}^{-2}$, demonstrating outstanding long-term stability in a harsh seawater environment ([Figure 3.22d](#)).

Moreover, several studies exhibit either Cl^- corrosion or Cl_2 evolution in similar seawater-like conditions, whereas B,Al-NiFe LDH demonstrated high chloride tolerance and oxygen selectivity, as confirmed by the potassium iodide-starch paper test ([Figure 3.23](#)).^{78,79} These comparisons underscore the advantage of Al incorporation in suppressing chloride-related degradation and highlight the effectiveness of B doping in sustaining high OER activity under corrosive conditions.²²

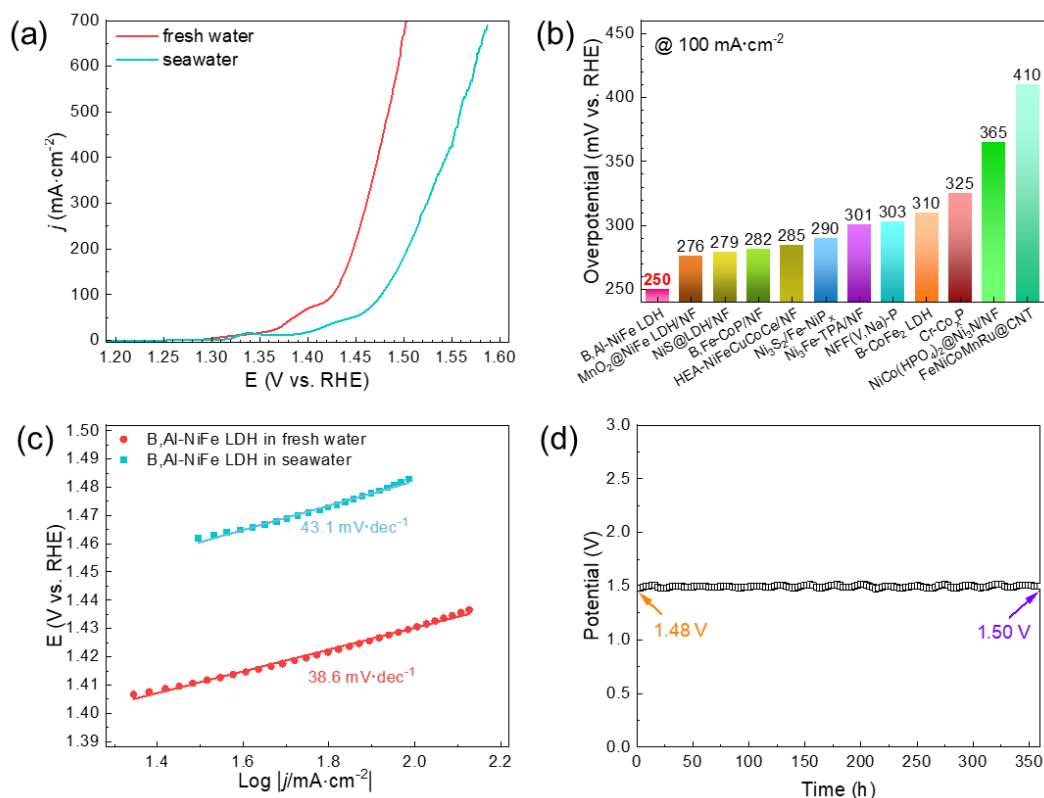


Figure 3.22 Application of B₂Al-NiFe LDH in alkaline natural seawater (1 M KOH + seawater): (a) the polarization comparison of B₂Al-NiFe LDH between electrolytes of 1 M KOH and 1 M KOH + seawater, (b) the comparison to the state-of-the-art electrocatalysts in alkaline seawater splitting, (c) the Tafel slopes calculated from curves in [Figure 3.22a](#), (d) the CP stability measurement run at 100 mA·cm⁻².



Figure 3.23 Digital photo of potassium iodide-starch paper with seawater electrolyte after running for 360 hours at the current density of 100 mA·cm⁻², and comparison with water, and solution containing Cl₂.

Table 3.5 The comparison of B,Al-NiFe LDH with recent publications on overpotential @ 100 mA·cm⁻²

Samples	Overpotential (mV) @100 mA·cm ⁻²	References
B,Al-NiFe LDH	250	This work
MnO ₂ @NiFe LDH/NF	276	77
S-NiFe LDH	237	80
B,Fe-CoP/NF	282	25
Cr-CoxP	325	81
NiCo(HPO ₄) ₂ @Ni ₃ N/NF	365	82
NFF(V, Na)-P	303	83
NiS@LDH/NF	279	84
Ni ₃ Fe-TPA/NF	301	85
HEA-NiFeCuCoCe/NF	285	86
FeNiCoMnRu@CNT	410	87
Ni ₃ S ₂ /Fe-NiPx	290	42
B-CoFe ₂ LDH	310	23

3.3.5 Performance of AEMWE and AEMSE Single Cells

To assess the practical applicability of the B,Al-NiFe LDH catalyst, we assembled and evaluated anion exchange membrane water electrolyzer (AEMWE) and anion exchange membrane seawater electrolyzer (AEMSE) single cells under ambient conditions. A 1 × 1 cm² NF electrode coated with B,Al-NiFe LDH served as the anode, paired with a commercial Pt/C cathode (B,Al-NiFe||Pt/C). For benchmarking, identical cells using commercial RuO₂ as the anode (RuO₂||Pt/C) were fabricated.

As shown in [Figure 3.24a](#), the B,Al-NiFe||Pt/C configuration exhibits remarkable activity in 1 M KOH, requiring cell voltages of 1.60, 1.66, and 1.71 V to achieve current densities of 100, 200, and 400 mA·cm⁻², respectively. In contrast, the RuO₂||Pt/C cell requires significantly higher voltages of 1.65, 1.82, and 2.11 V at the same current densities ([Figure 3.24b](#)). Notably, the performance gap between B,Al-NiFe and RuO₂ widens with increasing current density, growing from 50 mV at 100 mA·cm⁻² to 400 mV

at 400 mA·cm⁻², indicating that B₂Al-NiFe LDH performs particularly well under high current operating conditions. Furthermore, we compared our results with the state-of-the-art AEMWE cells ([Figure 3.24c](#), [Table 3.6](#)). The B₂Al-NiFePt/C cell exhibits consistently lower operating voltages across all tested current densities, and shows the lowest reported potential at 400 mA·cm⁻² among comparable systems, highlighting its promising scalability for industrial hydrogen production.

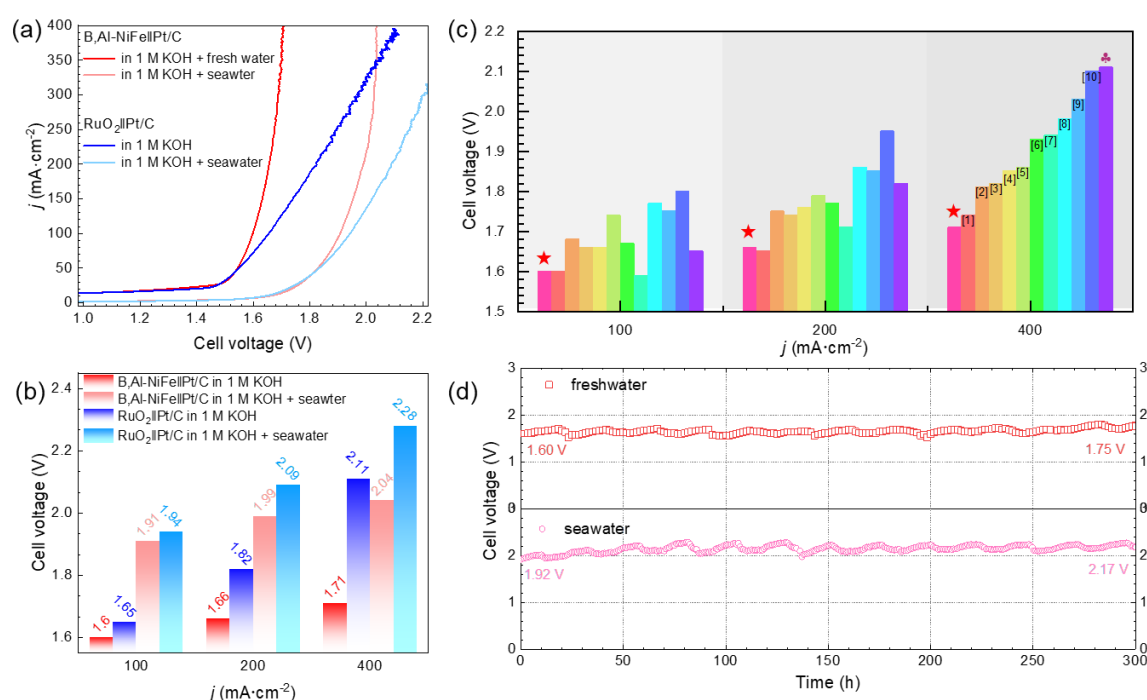


Figure 3.24 Evaluation of AEMWE and AEMSE in 1 M KOH or 1 M KOH + seawater, respectively: (a) polarization curves of B₂Al-NiFePt/C and RuO₂Pt/C, (b) the required cell voltages at current densities of 100, 200, 400 mA·cm⁻², (c) the comparison to the state-of-the-art AEMWE (listed in [Table S6](#)), (d) the CP stability of B₂Al-NiFePt/C in freshwater and seawater at current density of 100 mA·cm⁻².

A similar trend was observed during seawater electrolysis ([Figure 3.24a, b](#)). For both B₂Al-NiFePt/C cell, higher cell voltage was required compared to freshwater, with the voltage gap reaching a maximum of ~300 mV at 400 mA·cm⁻². This increase is likely attributed to the seawater-induced effects, such as ion adsorption, and possible interface polarization, which can negatively impact electrode kinetics. Nonetheless,

B,Al-NiFe//Pt/C maintains excellent performance, requiring only 1.91, 1.99, and 2.04 V to achieve 100, 200, and 400 mA·cm⁻², respectively, while RuO₂//Pt/C again requires higher voltages (1.94, 2.09, and 2.28, respectively). These results confirm the superior seawater OER capability of B,Al-NiFe LDH.

Long-term CP tests at 100 mA·cm⁻² were conducted to evaluate operational stability ([Figure 3.24d](#)). In 1 M KOH, the B,Al-NiFe//Pt/C cell exhibits excellent stability, with a cell voltage increase of 50 mV over 300 hours, corresponding to a ~8.6% degradation. As for the stability in seawater, the B,Al-NiFe//Pt/C cell shows a voltage increase from 1.92 to 2.17 V at a constant current density of 100 mA·cm⁻², which corresponds to a 13% increase, which is higher than the one in freshwater and the value (~1.5%) in [Figure 3.22d](#), possibly due to the degradation of cathodic Pt/C.

Table 3.6 The comparison among as-assembled B,Al-NiFe LDH//Pt/C, RuO₂//Pt/C in freshwater with the state-of-the-art.

	AEMWE	Applied voltage (V)			References
		@ 100 mA·cm ⁻²	@ 200 mA·cm ⁻²	@ 400 mA·cm ⁻²	
★	B,Al-NiFe LDH // Pt/C	1.61	1.68	1.73	This work
[1]	NiFeOOH // B, V-Ni ₂ P	1.60	1.65	1.74	88
[2]	NiFe LDH/Ni ₄ Mo // NiFe LDH/Ni ₄ Mo	1.68	1.75	1.81	10
[3]	Ni(Cu)Fe/NF // Ni(Cu)Fe/NF	1.66	1.74	1.82	89
[4]	Mil53-HE // Mil53-HE	1.66	1.76	1.85	90
[5]	NiFe-W _x /NF // NiFe-W _x /NF	1.74	1.79	1.86	91
[6]	NiFeMo(OH) ₂ // Pt/C	1.67	1.77	1.93	19
[7]	Ni-Fe-C // Pt/C	1.59	1.71	1.94	92
[8]	Cu _{0.81} Co _{2.19} O ₄ NS/NF // Co ₃ O ₄	1.77	1.86	1.98	93
[9]	C-IL-100 // NiFe ₂ O ₄ CP	1.75	1.85	2.03	94
[10]	NiFeCr-LDH // NiMoCo	1.8	1.95	2.10	95
♣	RuO ₂ // Pt/C	1.65	1.82	2.11	This work

Based on the above, the direct comparison between B,Al-NiFe//Pt/C and RuO₂//Pt/C

cells clearly demonstrates the superior catalytic activity and stability of B,Al-NiFe LDH grown on NF. The combination of low operating voltages, high current density performance, and excellent long-term stability in both freshwater and seawater underscores its strong potential as a scalable electrocatalyst for green hydrogen production.

3.4 Conclusions

In this study, we present a rational dual-doping strategy to engineer NiFe-based LDH nanosheets as advanced electrocatalysts for OER. By co-incorporating B and Al into the NiFe LDH lattice, we achieve electronic band structure modulation and optimized adsorption of oxygenated intermediates, effectively steering the reaction pathway toward the LOM over the conventional AEM.

Experimental data and DFT simulations confirm the synergistic effect of B and Al. Specifically, B doping induces strong M-B interactions that facilitate charge redistribution, promoting electronic structure modulation favorable for catalytic performance, while Al doping enhances the structure integrity of LDH lattice, thereby enhancing the long-term stability. As a result, electrochemical measurements reveal that B,Al-NiFe LDH achieves outstanding intrinsic OER activity, with overpotentials as low as 169, 196, and 254 mV in 1 M KOH at current densities of 10, 100, and 500 $\text{mA}\cdot\text{cm}^{-2}$, respectively. Beyond its high electrocatalytic activity, the catalyst retains over 98.6% of its initial performance after 360 hours at 100 $\text{mA}\cdot\text{cm}^{-2}$, demonstrating excellent long-term stability. When integrated into AEMWE and AEMSE single cells, the B,Al-NiFe||Pt/C cell retains high activity and selectivity for oxygen evolution, effectively suppressing chloride evolution. Under seawater electrolysis at 100 $\text{mA}\cdot\text{cm}^{-2}$, the cell voltage increased by 13% after 300 hours of continuous operation, underscoring its durability in harsh environments. Compared to state-of-the-art alkaline water electrocatalysts, B,Al-NiFe LDH exhibits superior performance across a wide current density range up to 400 $\text{mA}\cdot\text{cm}^{-2}$, even outperforming benchmark configurations under identical testing conditions.

This work not only provides valuable insight into dopant-induced electronic modulation in LDH but also offers a promising strategy for designing high-performance, earth-abundant OER electrocatalysts. Moreover, the results clearly demonstrate the potential of this material for practical applications in sustainable hydrogen production from both freshwater and seawater electrolysis.

3.5 References

- 1 Service, R. F. The parting of water. *Science* **2025**, 387 (6732), 354-357. <https://doi.org/10.1126/science.adw0390>.
- 2 Xie, X.; Du, L.; Yan, L.; Park, S.; Qiu, Y.; Sokolowski, J.; Wang, W.; Shao, Y. Oxygen evolution reaction in alkaline environment: material challenges and solutions. *Advanced Functional Materials* **2022**, 32 (21), 2110036. <https://doi.org/10.1002/adfm.202110036>.
- 3 Shi, Q.; Zhu, C.; Du, D.; Lin, Y. Robust noble metal-based electrocatalysts for oxygen evolution reaction. *Chemical Society Reviews* **2019**, 48 (12), 3181-3192. <https://doi.org/10.1039/c8cs00671g>.
- 4 Wang, H.; Yan, Z.; Cheng, F.; Chen, J. Advances in noble metal electrocatalysts for acidic oxygen evolution reaction: construction of under-coordinated active sites. *Advanced Science* **2024**, 11 (32), 2401652. <https://doi.org/10.1002/advs.202401652>.
- 5 Qin, R.; Chen, G.; Feng, X.; Weng, J.; Han, Y. Ru/Ir-based electrocatalysts for oxygen evolution reaction in acidic conditions: from mechanisms, optimizations to challenges. *Advanced Science* **2024**, 11 (21), 2309364. <https://doi.org/10.1002/advs.202309364>.
- 6 Feng, Z.; Dai, C.; Shi, P.; Lei, X.; Guo, R.; Wang, B.; Liu, X.; You, J. Seven mechanisms of oxygen evolution reaction proposed recently: a mini review. *Chemical Engineering Journal* **2024**, 485, 149992. <https://doi.org/10.1016/j.cej.2024.149992>.
- 7 Zhang, N.; Xiong, Y. Lattice oxygen activation for enhanced electrochemical oxygen evolution. *The Journal of Physical Chemistry C* **2023**, 127 (5), 2147-2159. <https://doi.org/10.1021/acs.jpcc.2c08514>.
- 8 Zhang, N.; Feng, X.; Rao, D.; Deng, X.; Cai, L.; Qiu, B.; Long, R.; Xiong, Y.; Lu, Y.; Chai, Y. Lattice oxygen activation enabled by high-valence metal sites for enhanced water oxidation. *Nature Communications* **2020**, 11 (1). <https://doi.org/10.1038/s41467-020-17934-7>.
- 9 Zhou, D.; Li, P.; Lin, X.; McKinley, A.; Kuang, Y.; Liu, W.; Lin, W.-F.; Sun, X.; Duan, X. Layered double hydroxide-based electrocatalysts for the oxygen evolution reaction: identification and tailoring of active sites, and superaerophobic nanoarray electrode assembly. *Chemical Society Reviews* **2021**, 50 (15), 8790-8817. <https://doi.org/10.1039/d1cs00186h>.
- 10 Wu, F.; Tian, F.; Li, M.; Geng, S.; Qiu, L.; He, L.; Li, L.; Chen, Z.; Yu, Y.; Yang, W.; Hou, Y. Engineering lattice oxygen regeneration of NiFe layered double hydroxide enhances oxygen evolution catalysis durability. *Angewandte Chemie International Edition* **2024**, 64 (1), 2413250. <https://doi.org/10.1002/anie.202413250>.
- 11 Han, Y.; Wang, J.; Liu, Y.; Li, T.; Wang, T.; Li, X.; Ye, X.; Li, G.; Li, J.; Hu, W.; Deng, Y. Stability challenges and opportunities of NiFe-based electrocatalysts for oxygen evolution reaction in alkaline media. *Carbon Neutralization* **2024**, 3 (2), 172-198. <https://doi.org/10.1002/cnl2.110>.
- 12 Tucker-Quinónez, A. M.; Rivadeneira-Mendoza, B. F.; Gorozabel-Mendoza, M. L.; Pérez-Almeida, I. B.; García-Guerrero, A. J.; Dueñas-Rivadeneira, A. A.; Yadav, K. K.; Zambrano-Intriago, L. A.; Rodríguez-Díaz, J. M. Challenges and potential of layered double hydroxides as electrocatalytic materials for hydrogen production from water: a review of recent advances and applications. *Energy Nexus* **2025**, 17, 100399. <https://doi.org/10.1016/j.nexus.2025.100399>.
- 13 Chen, R.; Hung, S.; Zhou, D.; Gao, J.; Yang, C.; Tao, H.; Yang, H. B.; Zhang, L.; Zhang, L.; Xiong, Q.; Chen, H. M.; Liu, B. Layered structure causes bulk NiFe layered double hydroxide unstable in alkaline oxygen evolution reaction. *Advanced Materials* **2019**, 31 (41), 1903909. <https://doi.org/10.1002/adma.201903909>.
- 14 Yan, Y.; Lin, J.; Huang, K.; Zheng, X.; Qiao, L.; Liu, S.; Cao, J.; Jun, S. C.; Yamauchi, Y.; Qi, J.

Tensile strain-mediated spinel ferrites enable superior oxygen evolution activity. *Journal of the American Chemical Society* **2023**, *145* (44), 24218-24229. <https://doi.org/10.1021/jacs.3c08598>.

- 15 Wang, Y.; Li, L.; Shi, J.; Xie, M.; Nie, J.; Huang, G.; Li, B.; Hu, W.; Pan, A.; Huang, W. Oxygen defect engineering promotes synergy between adsorbate evolution and single lattice oxygen mechanisms of OER in transition metal-based (oxy)hydroxide. *Advanced Science* **2023**, *10* (32). <https://doi.org/10.1002/advs.202303321>.
- 16 Wang, T.; Guo, M.; Zhang, X.; Cao, Y.; Wu, Q.; Tu, J.; Zhang, K. Defect-rich NiFeAl-layered double hydroxide nanosheets for efficient electrocatalytic oxygen evolution reaction. *ACS Applied Nano Materials* **2023**, *6* (7), 6002-6010. <https://doi.org/10.1021/acsanm.3c00356>.
- 17 Zhu, Y.; Wang, J.; Weiser, G.; Klingenhof, M.; Koketsu, T.; Liu, S.; Pi, Y.; Henkelman, G.; Shi, X.; Li, J.; Pao, C.; Yeh, M.; Huang, W.; Strasser, P.; Ma, J. Ru single atoms and sulfur anions dual-doped NiFe layered double hydroxides for high-current-density alkaline oxygen evolution reaction. *Advanced Energy Materials* **2025**, *15* (23), 2500554. <https://doi.org/10.1002/aenm.202500554>.
- 18 Zhang, H.; Zhou, H.; Wang, H.; Wang, Y.; Yang, X.; Wu, D.; Yuan, P.; He, M.; Wei, W.; Yang, T. Multihybridization for enhancing Fe-Ni bimetal electrocatalyst in water oxidation. *Advanced Energy Materials* **2025**, *15* (13), 2403464. <https://doi.org/10.1002/aenm.202403464>.
- 19 Wang, J.; Xing, Z.; Kang, R.; Zheng, Y.; Zhang, Z.; Ma, T.; Wang, Y.; Yin, B.; Liao, Y.; Li, L.; Cheng, C.; Li, S. Metal nitride controlled atomic doping of Mo^{x+} in NiFe (oxy)hydroxide to trigger lattice oxygen-mediated mechanism for superior oxygen evolution. *Advanced Functional Materials* **2024**, *35* (14), 2418439. <https://doi.org/10.1002/adfm.202418439>.
- 20 Zhou, Y.-N.; Yu, W.-L.; Cao, Y.-N.; Zhao, J.; Dong, B.; Ma, Y.; Wang, F.-L.; Fan, R.-Y.; Zhou, Y.-L.; Chai, Y.-M. S-doped nickel-iron hydroxides synthesized by room-temperature electrochemical activation for efficient oxygen evolution. *Applied Catalysis B Environment and Energy* **2021**, *292*, 120150. <https://doi.org/10.1016/j.apcatb.2021.120150>.
- 21 Guan, S.; Xu, B.; Yu, X.; Ye, Y.; Liu, Y.; Guan, T.; Yang, Y.; Gao, J.; Li, K.; Wang, J. Activation of lattice oxygen in nitrogen-doped high-entropy oxide nanosheets for highly efficient oxygen evolution reaction. *ACS Catalysis* **2024**, *14* (23), 17806-17817. <https://doi.org/10.1021/acscatal.4c05997>.
- 22 Liu, W.; Yu, J.; Li, T.; Li, S.; Ding, B.; Guo, X.; Cao, A.; Sha, Q.; Zhou, D.; Kuang, Y.; Sun, X. Self-protecting CoFeAl-layered double hydroxides enable stable and efficient brine oxidation at 2 A cm⁻². *Nature Communications* **2024**, *15*, 4712. <https://doi.org/10.1038/s41467-024-49195-z>.
- 23 Wu, L.; Yu, L.; Zhu, Q.; McElhenny, B.; Zhang, F.; Wu, C.; Xing, X.; Bao, J.; Chen, S.; Ren, Z. Boron-modified cobalt iron layered double hydroxides for high efficiency seawater oxidation. *Nano Energy* **2021**, *83*, 105838. <https://doi.org/10.1016/j.nanoen.2021.105838>.
- 24 R, N. K. T.; Kamalakannan, S.; Prakash, M.; Viswanathan, B.; Neppolian, B. Boron-induced cationic vacancy on copper cobalt oxide toward formate selectivity: new insights into methanol oxidation reaction. *ACS Applied Energy Materials* **2022**, *5* (2), 2104-2111. <https://doi.org/10.1021/acsaem.1c03643>.
- 25 Pan, Y.; Wang, Z.; Wang, K.; Ye, Q.; Shen, B.; Yang, F.; Cheng, Y. Dual doping of B and Fe activated lattice oxygen participation for enhanced oxygen evolution reaction activity in alkaline freshwater and seawater. *Advanced Functional Materials* **2024**, *34* (37), 2402264. <https://doi.org/10.1002/adfm.202402264>.
- 26 Kou, C.; Zhou, J.; Wang, H.; Han, J.; Han, M.; Vomiero, A.; Liu, Y.; Liang, H. Boron pretreatment promotes phosphorization of FeNi catalysts for oxygen evolution. *Applied Catalysis B: Environment and Energy* **2023**, *330*, 122598. <https://doi.org/10.1016/j.apcatb.2023.122598>.

- 27 Vos, J. G.; Liu, Z.; Speck, F. D.; Perini, N.; Fu, W.; Cherevko, S.; Koper, M. T. M. Selectivity trends between oxygen evolution and chlorine evolution on iridium-based double perovskites in acidic media. *ACS Catalysis* **2019**, *9* (9), 8561-8574. <https://doi.org/10.1021/acscatal.9b01159>.
- 28 Zhang, R.; Zhai, T.; Wang, H.; Lu, S. Recent advances in high-performance direct seawater electrolysis for “Green” hydrogen. *Advanced Energy and Sustainability Research* **2024**, *5* (9), 2400085. <https://doi.org/10.1002/aesr.202400085>.
- 29 Tong, W.; Forster, M.; Dionigi, F.; Dresch, S.; Erami, R. S.; Strasser, P.; Cowan, A. J.; Farràs, P. Electrolysis of low-grade and saline surface water. *Nature Energy* **2020**, *5* (5), 367-377. <https://doi.org/10.1038/s41560-020-0550-8>.
- 30 Li, Y.; Guo, H.; Zhao, J.; Pang, K.; Song, R. Rapid surface reconstruction of Te-doped NiFe layered double hydroxide for robust oxygen evolution at high current density. *ACS Sustainable Chemistry & Engineering* **2024**, *12* (32), 12101-12112. <https://doi.org/10.1021/acssuschemeng.4c03672>.
- 31 Kresse, G.; Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Computational Materials Science* **1996**, *6* (1), 15-50. [https://doi.org/10.1016/0927-0256\(96\)00008-0](https://doi.org/10.1016/0927-0256(96)00008-0).
- 32 Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Physical Review. B, Condensed Matter* **1996**, *54* (16), 11169-11186. <https://doi.org/10.1103/physrevb.54.11169>.
- 33 Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Physical Review Letters* **1996**, *77* (18), 3865-3868. <https://doi.org/10.1103/physrevlett.77.3865>.
- 34 Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Physical Review. B, Condensed Matter* **1999**, *59* (3), 1758-1775. <https://doi.org/10.1103/physrevb.59.1758>.
- 35 Blöchl, P. E. Projector augmented-wave method. *Physical Review. B, Condensed Matter* **1994**, *50* (24), 17953-17979. <https://doi.org/10.1103/physrevb.50.17953>.
- 36 Monkhorst, H. J.; Pack, J. D. Special points for Brillouin-zone integrations. *Physical Review. B, Solid State* **1976**, *13* (12), 5188-5192. <https://doi.org/10.1103/physrevb.13.5188>.
- 37 Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the damping function in dispersion corrected density functional theory. *Journal of Computational Chemistry* **2011**, *32* (7), 1456-1465. <https://doi.org/10.1002/jcc.21759>.
- 38 Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *The Journal of Chemical Physics* **2010**, *132* (15). <https://doi.org/10.1063/1.3382344>.
- 39 Lee, B.-J.; Jung, S.-M.; Yu, G.; Kim, H.-Y.; Kwon, J.; Kim, K.-S.; Kwak, J.; Lee, W.; Mok, D. H.; Back, S.; Kim, Y.-T. Highly active and stable Al-doped NiFe self-supported oxygen evolution reaction electrode for alkaline water electrolysis. *ACS Catalysis* **2025**, *15* (2), 1123-1134. <https://doi.org/10.1021/acscatal.4c04393>.
- 40 Yang, C.; Zhu, Y.; Zhang, F.; Yao, L.; Chen, Y.; Lu, T.; Li, Q.; Li, J.; Wang, G.; Cheng, Q.; Yang, H. Sulfur-doped IrO₂ enable pathway switch to lattice oxygen mechanism with enhanced stability for low iridium PEM water electrolysis. *Advanced Materials* **2025**. <https://doi.org/10.1002/adma.202507560>.
- 41 Fang, Q.; Wang, L.; Yang, D.; Xue, L.; Gu, W.; Hu, L.; Shi, L.; Zhu, C. Ga-induced p-d orbital hybridization in CoFe LDH for boosted oxygen evolution electrocatalysis. *ACS Materials Letters* **2024**, *6* (9), 3963-3969. <https://doi.org/10.1021/acsmaterialslett.4c01197>.
- 42 Luo, X.; Ji, P.; Wang, P.; Tan, X.; Chen, L.; Mu, S. Spherical Ni₃S₂/Fe-NiP_x magic cube with

- ultrahigh water/seawater oxidation efficiency. *Advanced Science* **2022**, 9 (7), 2104846. <https://doi.org/10.1002/advs.202104846>.
- 43 Deng, X.; Wang, S.; Liu, Y.; Cao, J.; Huang, J.; Shi, X. Sulfidation and NaOH etching in CoFeAl LDH evolved catalysts for an efficient overall water splitting in an alkaline solution. *Nanoscale* **2023**, 15 (20), 9049-9059. <https://doi.org/10.1039/d3nr01276j>.
 - 44 Wang, Z.; Niu, X.; Ye, L.; Wang, X.; Wang, C.; Wen, Y.; Zong, L.; Wang, L.; Gao, H.; Li, X.; Zhan, T. Boron modification promoting electrochemical surface reconstruction of NiFe-LDH for efficient and stable freshwater/seawater oxidation catalysis. *Journal of Colloid and Interface Science* **2024**, 668, 607-617. <https://doi.org/10.1016/j.jcis.2024.04.198>.
 - 45 Liu, L.; Tang, Y.; Liu, S.; Yu, M.; Sun, Y.; Fu, X.; Luo, J.; Liu, S. Unraveling the trade-off between oxygen vacancy concentration and ordering of perovskite oxides for efficient lattice oxygen evolution. *Advanced Energy Materials* **2024**, 15 (5), 2402967. <https://doi.org/10.1002/aenm.202402967>.
 - 46 Li, C.; Xie, L.; Zhao, J.; Gu, L.; Tang, H.; Zheng, L.; Li, G. Interfacial Fe-O-Ni-O-Fe bonding regulates the active Ni sites of Ni-MOFs via iron doping and decorating with FeOOH for super-efficient oxygen evolution. *Angewandte Chemie International Edition* **2022**, 61 (17), 2116934. <https://doi.org/10.1002/anie.202116934>.
 - 47 Lin, Z.; Bu, P.; Xiao, Y.; Gao, Q.; Diao, P. β - and γ -NiFeOOH electrocatalysts for an efficient oxygen evolution reaction: an electrochemical activation energy aspect. *Journal of Materials Chemistry A* **2022**, 10 (39), 20847-20855. <https://doi.org/10.1039/d2ta04688a>.
 - 48 Jiang, J.; Sun, F.; Zhou, S.; Hu, W.; Zhang, H.; Dong, J.; Jiang, Z.; Zhao, J.; Li, J.; Yan, W.; Wang, M. Atomic-level insight into super-efficient electrocatalytic oxygen evolution on iron and vanadium co-doped nickel (oxy)hydroxide. *Nature Communications* **2018**, 9, 2885. <https://doi.org/10.1038/s41467-018-05341-y>.
 - 49 Zhu, Z.; Xu, K.; Guo, W.; Zhang, H.; Xiao, X.; He, M.; Yu, T.; Zhao, H.; Zhang, D.; Yang, T. Vanadium-phosphorus incorporation induced interfacial modification on cobalt catalyst and its super electrocatalysis for water splitting in alkaline media. *Applied Catalysis B: Environment and Energy* **2021**, 304, 120985. <https://doi.org/10.1016/j.apcatb.2021.120985>.
 - 50 Wang, D.; Li, Q.; Han, C.; Lu, Q.; Xing, Z.; Yang, X. Atomic and electronic modulation of self-supported nickel-vanadium layered double hydroxide to accelerate water splitting kinetics. *Nature Communications* **2019**, 10, 2899. <https://doi.org/10.1038/s41467-019-11765-x>.
 - 51 Huang, L.; Gao, G.; Zhang, H.; Chen, J.; Fang, Y.; Dong, S. Self-dissociation-assembly of ultrathin metal-organic framework nanosheet arrays for efficient oxygen evolution. *Nano Energy* **2019**, 68, 104296. <https://doi.org/10.1016/j.nanoen.2019.104296>.
 - 52 Yu, L.; Zhu, Q.; Song, S.; McElhenny, B.; Wang, D.; Wu, C.; Qin, Z.; Bao, J.; Yu, Y.; Chen, S.; Ren, Z. Non-noble metal-nitride based electrocatalysts for high-performance alkaline seawater electrolysis. *Nature Communications* **2019**, 10, 5106. <https://doi.org/10.1038/s41467-019-13092-7>.
 - 53 Mavel, G.; Escard, J.; Costa, P.; Castaing, J. ESCA surface study of metal borides. *Surface Science* **1973**, 35, 109-116. [https://doi.org/10.1016/0039-6028\(73\)90207-0](https://doi.org/10.1016/0039-6028(73)90207-0).
 - 54 Fan, Y.; Zhang, C.; Zhang, L.; Zhou, J.; Li, Y.; Huang, Y.-C.; Ma, J.; Chan, T.-S.; Chen, C.-T.; Jing, C.; Mijit, E.; Hu, Z.; Wang, J.-Q.; Zhang, L. Novel mechanism of Fe⁴⁺/Ni³⁺ synergistic effect via exchange energy gain for boosting water oxidation. *Chem Catalysis* **2024**, 4 (5), 100981. <https://doi.org/10.1016/j.checat.2024.100981>.
 - 55 Xiang, W.; Hernandez, S.; Hosseini, P.; Bai, F.; Hagemann, U.; Heidelmann, M.; Li, T. Unveiling surface species formed on Ni-Fe spinel oxides during the oxygen evolution reaction at the atomic scale. *Advanced Science* **2025**, 12 (25), 2501967. <https://doi.org/10.1002/advs.202501967>.

- 56 Idriss, H. On the wrong assignment of the XPS O1s signal at 531-532 eV attributed to oxygen vacancies in photo- and electro-catalysts for water splitting and other materials applications. *Surface Science* **2021**, 712, 121894. <https://doi.org/10.1016/j.susc.2021.121894>.
- 57 Feng, F.; Zeng, Y.; Yan, D.; Ren, Q.; Lan, B.; Zhong, J.; Liu, B.; Dong, T.; Huang, H. Construction of hollow sphere MnO_x with abundant oxygen vacancy for accelerating VOCs degradation: Investigation through operando spectroscopy combined with on-line mass spectrometry. *Journal of Colloid and Interface Science* **2024**, 673, 746–755. <https://doi.org/10.1016/j.jcis.2024.06.117>.
- 58 Hoch, L. B.; Wood, T. E.; O'Brien, P. G.; Liao, K.; Reyes, L. M.; Mims, C. A.; Ozin, G. A. The rational design of a single-component photocatalyst for gas-phase CO₂ reduction using both UV and visible light. *Advanced Science* **2014**, 1 (1): 1400013. <https://doi.org/10.1002/advs.201400013>.
- 59 Gnanamani, M. K.; Rajabathar, J. R. Defects chemistry and catalysis of Indium oxide. In *Elsevier eBooks*; **2023**; pp 665-690. <https://doi.org/10.1016/b978-0-323-85588-4.00004-0>.
- 60 Zhao, S.; Li, K.; Jiang, S.; Li, J. Pd-Co based spinel oxides derived from pd nanoparticles immobilized on layered double hydroxides for toluene combustion. *Applied Catalysis B: Environment and Energy* **2015**, 181, 236-248. <https://doi.org/10.1016/j.apcatb.2015.08.001>.
- 61 Zeng, Y.; Li, T.; Zhong, J.; Mao, H.; Fu, M.; Ye, D.; Hu, Y. Unraveling the role of Co₃O₄ facet for photothermal catalytic oxidation of methanol via operando spectroscopy and theoretical investigation. *Journal of Colloid and Interface Science* **2023**, 643, 360-372. <https://doi.org/10.1016/j.jcis.2023.04.046>.
- 62 Ciftiyurek, E.; Li, Z.; Schierbaum, K. Adsorbed oxygen ions and oxygen vacancies: their concentration and distribution in metal oxide chemical sensors and influencing role in sensitivity and sensing mechanisms. *Sensors* **2022**, 23 (1): 29. <https://doi.org/10.3390/s23010029>.
- 63 Lu, R.; Zhang, X.; Shi, H.; Zhao, Z.; Li, M.; Zhang, X. Wettability control in electrocatalytic CO₂ reduction: effects, modulations and mechanisms. *Applied Catalysis B Environment and Energy* **2023**, 341, 123293. <https://doi.org/10.1016/j.apcatb.2023.123293>.
- 64 Zhang, F.; Zhao, R.; Wang, Y.; Han, L.; Gu, J.; Niu, Z.; Yuan, Y.; Qu, N.; Meng, J.; Wang, D. Superwetable surface-dependent efficiently electrocatalytic water splitting based on their excellent liquid adsorption and gas desorption. *Chemical Engineering Journal* **2022**, 452, 139513. <https://doi.org/10.1016/j.cej.2022.139513>.
- 65 Jiang, S.; Xiao, T.; Xu, C.; Wang, S.; Peng, H.; Zhang, W.; Liu, B.; Song, Y. Passivating oxygen evolution activity of NiFe-LDH through heterostructure engineering to realize high-efficiency electrocatalytic formate and hydrogen co-production. *Small* **2023**, 19 (27), 2208027. <https://doi.org/10.1002/sml.202208027>.
- 66 Cai, M.; Zhu, Q.; Wang, X.; Shao, Z.; Yao, L.; Zeng, H.; Wu, X.; Chen, J.; Huang, K.; Feng, S. Formation and stabilization of NiOOH by introducing α-FeOOH in LDH: composite electrocatalyst for oxygen evolution and urea oxidation reactions. *Advanced Materials* **2022**, 35 (7), 2209338. <https://doi.org/10.1002/adma.202209338>.
- 67 Huang, Z.-F.; Xi, S.; Song, J.; Dou, S.; Li, X.; Du, Y.; Diao, C.; Xu, Z. J.; Wang, X. Tuning of lattice oxygen reactivity and scaling relation to construct better oxygen evolution electrocatalyst. *Nature Communications* **2021**, 12, 3992. <https://doi.org/10.1038/s41467-021-24182-w>.
- 68 Wu, Y.; Zhao, Y.; Zhai, P.; Wang, C.; Gao, J.; Sun, L.; Hou, J. Triggering lattice oxygen activation of single - atomic Mo sites anchored on Ni-Fe oxyhydroxides nanoarrays for electrochemical water oxidation. *Advanced Materials* **2022**, 34 (29), 2202523. <https://doi.org/10.1002/adma.202202523>.

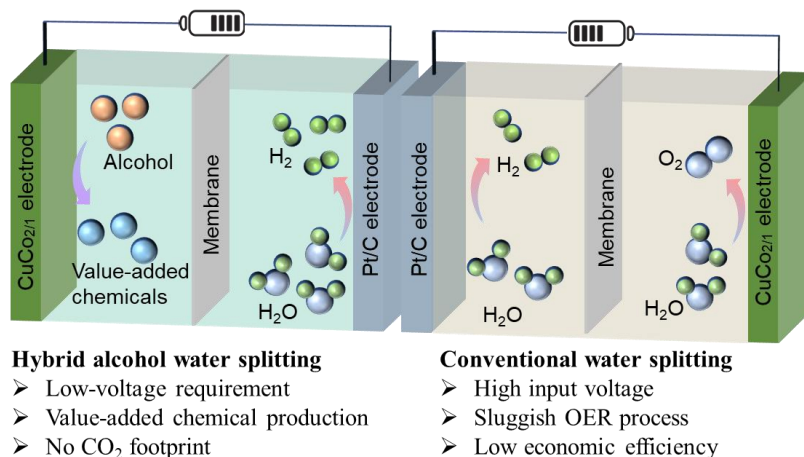
- 69 Jia, H.; Yao, N.; Yu, C.; Cong, H.; Luo, W. Unveiling the electrolyte cations dependent kinetics on CoOOH-catalyzed oxygen evolution reaction. *Angewandte Chemie International Edition* **2023**, 62 (49), 2313886. <https://doi.org/10.1002/anie.202313886>.
- 70 Exner, K. S.; Over, H. Beyond the rate-determining step in the oxygen evolution reaction over a single-crystalline IrO₂(110) model electrode: kinetic scaling relations. *ACS Catalysis* **2019**, 9 (8), 6755-6765. <https://doi.org/10.1021/acscatal.9b01564>.
- 71 Huang, Z.-F.; Song, J.; Du, Y.; Xi, S.; Dou, S.; Nsanzimana, J. M. V.; Wang, C.; Xu, Z. J.; Wang, X. Chemical and structural origin of lattice oxygen oxidation in Co-Zn oxyhydroxide oxygen evolution electrocatalysts. *Nature Energy* **2019**, 4 (4), 329-338. <https://doi.org/10.1038/s41560-019-0355-9>.
- 72 Xiao, K.; Wang, Y.; Wu, P.; Hou, L.; Liu, Z. Activating lattice oxygen in spinel ZnCo₂O₄ through filling oxygen vacancies with fluorine for electrocatalytic oxygen evolution. *Angewandte Chemie International Edition* **2023**, 62 (24), 2301408. <https://doi.org/10.1002/anie.202301408>.
- 73 Pan, Y.; Xu, X.; Zhong, Y.; Ge, L.; Chen, Y.; Veder, J.-P. M.; Guan, D.; O'Hayre, R.; Li, M.; Wang, G.; Wang, H.; Zhou, W.; Shao, Z. Direct evidence of boosted oxygen evolution over perovskite by enhanced lattice oxygen participation. *Nature Communications* **2020**, 11, 2002. <https://doi.org/10.1038/s41467-020-15873-x>.
- 74 Tomar, A. K.; Pan, U. N.; Kim, N. H.; Lee, J. H. Enabling lattice oxygen participation in a triple perovskite oxide electrocatalyst for the oxygen evolution reaction. *ACS Energy Letters* **2022**, 8 (1), 565-573. <https://doi.org/10.1021/acsenenergylett.2c02617>.
- 75 Zhang, T.; Zhao, H.-F.; Chen, Z.-J.; Yang, Q.; Gao, N.; Li, L.; Luo, N.; Zheng, J.; Bao, S.-D.; Peng, J.; Peng, X.; Liu, X.-W.; Yu, H.-B. High-entropy alloy enables multi-path electron synergism and lattice oxygen activation for enhanced oxygen evolution activity. *Nature Communications* **2025**, 16, 3327. <https://doi.org/10.1038/s41467-025-58648-y>.
- 76 Zhang, M.; De Respinis, M.; Frei, H. Time-resolved observations of water oxidation intermediates on a cobalt oxide nanoparticle catalyst. *Nature Chemistry* **2014**, 6 (4), 362-367. <https://doi.org/10.1038/nchem.1874>.
- 77 Tang, X.; Yang, N.; Li, Z.; Cai, Z.; Dai, Q.; Wang, H.; He, X.; Yao, Y.; Li, T.; Guo, J.; Niu, X.; Sun, X. NiFe-based arrays with manganese dioxide enhance chloride blocking for durable alkaline seawater oxidation. *Journal of Colloid and Interface Science* **2025**, 684, 64-72. <https://doi.org/10.1016/j.jcis.2025.01.106>.
- 78 Bahuguna, G.; Patolsky, F. Routes to avoiding chlorine evolution in seawater electrolysis: recent perspective and future directions. *ACS Materials Letters* **2024**, 6 (8), 3202-3217. <https://doi.org/10.1021/acsmaterialslett.4c00409>.
- 79 Gaur, A.; Enkhbayar, E.; Sharma, J.; Mhin, S.; Han, H. Chloride-Ion blocking in seawater electrolysis: narrating the tale of likes and dislikes between anode and ions. *Energy & Environment Materials* **2024**, 8 (1), e12817. <https://doi.org/10.1002/eem2.12817>.
- 80 Chen, Y.; Dong, L.; Jia, S.; Zhang, Q.; Liu, L.; Liu, Z.; Zhang, Z.; Yue, K.; Cheng, Y.; Li, D.; Zhu, Z.; Wang, Y. Superhydrophilic S-NiFe LDH by room temperature synthesis for enhanced alkaline water/seawater oxidation at large current densities. *Small* **2025**, 21 (9), 2409499. <https://doi.org/10.1002/smll.202409499>.
- 81 Song, Y.; Sun, M.; Zhang, S.; Zhang, X.; Yi, P.; Liu, J.; Huang, B.; Huang, M.; Zhang, L. Alleviating the work function of vein-like Co_xP by Cr doping for enhanced seawater electrolysis. *Advanced Functional Materials* **2023**, 33 (30), 2214081. <https://doi.org/10.1002/adfm.202214081>.
- 82 Sun, H.; Sun, J.; Song, Y.; Zhang, Y.; Qiu, Y.; Sun, M.; Tian, X.; Li, C.; Lv, Z.; Zhang, L. Nickel-cobalt hydrogen phosphate on nickel nitride supported on nickel foam for alkaline seawater electrolysis. *ACS Applied Materials & Interfaces* **2022**, 14 (19), 22061-22070.

<https://doi.org/10.1021/acsami.2c01643>.

- 83 Li, Y.; Jiang, J.; Wu, Q.; Feng, Y.; Chen, Z.; Xu, G.; Zhang, L. Vanadium-doped heterogeneous bimetallic phosphides derived from layered double hydroxides for saline water splitting. *Small* **2024**, *20* (40), 2402250. <https://doi.org/10.1002/sml.202402250>.
- 84 Ren, J.; Chen, L.; Tian, W.; Song, X.; Kong, Q.; Wang, H.; Yuan, Z. Rational synthesis of core-shell-structured nickel sulfide-based nanostructures for efficient seawater electrolysis. *Small* **2023**, *19* (27), 2300194. <https://doi.org/10.1002/sml.202300194>.
- 85 Xiao, L.; Bai, X.; Han, J.; Tang, T.; Chen, S.; Qi, H.; Hou, C.; Bai, F.; Wang, Z.; Guan, J. Surface reconstruction and structural transformation of two-dimensional Ni-Fe MOFs for oxygen evolution in seawater media. *Nano Research* **2023**, *17* (4), 2429-2437. <https://doi.org/10.1007/s12274-023-6088-x>.
- 86 Bian, H.; Qi, P.; Xie, G.; Liu, X.; Zeng, Y.; Zhang, D.; Wang, P. HEA-NiFeCuCoCe/NF through ultra-fast electrochemical self-reconstruction with high catalytic activity and corrosion resistance for seawater electrolysis. *Chemical Engineering Journal* **2023**, *477*, 147286. <https://doi.org/10.1016/j.cej.2023.147286>.
- 87 Zhang, Q.; Lian, K.; Liu, Q.; Qi, G.; Zhang, S.; Luo, J.; Liu, X. High entropy alloy nanoparticles as efficient catalysts for alkaline overall seawater splitting and Zn-air batteries. *Journal of Colloid and Interface Science* **2023**, *646*, 844-854. <https://doi.org/10.1016/j.jcis.2023.05.074>.
- 88 Zhao, T.; Wang, S.; Jia, C.; Rong, C.; Su, Z.; Dastafkan, K.; Zhang, Q.; Zhao, C. Cooperative boron and vanadium doping of nickel phosphides for hydrogen evolution in alkaline and anion exchange membrane water/seawater electrolyzers. *Small* **2023**, *19* (27), 2208076. <https://doi.org/10.1002/sml.202208076>.
- 89 Wang, H.; Liu, X.; Liu, G.; Wang, Y.; Du, X.; Li, J. Copper doping-induced high-valence nickel-iron-based electrocatalyst toward enhanced and durable oxygen evolution reaction. *Chem Catalysis* **2023**, *3* (3), 100552. <https://doi.org/10.1016/j.checat.2023.100552>.
- 90 Cheng, R.; He, X.; Ran, B.; Li, H.; Tang, W.; Sun, F.; Li, K.; Shao, X.; Chen, H.; Fu, C. High-entropy optimizing d-orbital electronic configuration of metal organic framework for high-current-density anion exchange membrane water electrolysis. *Nano Energy* **2024**, *134*, 110529. <https://doi.org/10.1016/j.nanoen.2024.110529>.
- 91 Sun, Y.; Yang, F.; Sun, S.; Wei, K.; Wang, Y.; Ma, G.; An, J.; Yuan, J.; Zhao, M.; Liu, J.; Liu, H.; Li, Y. Phase regulation of Ni(OH)₂ nanosheets induced by W doping as self-supporting electrodes for boosted water electrolysis. *Journal of Colloid and Interface Science* **2025**, *684*, 1-10. <https://doi.org/10.1016/j.jcis.2025.01.012>.
- 92 Ko, Y.-J.; Han, M. H.; Kim, H.; Kim, J.-Y.; Lee, W. H.; Kim, J.; Kwak, J. Y.; Kim, C.-H.; Park, T.-E.; Yu, S.-H.; Lee, W.-S.; Choi, C. H.; Strasser, P.; Oh, H.-S. Unraveling Ni-Fe 2D nanostructure with enhanced oxygen evolution via in situ and operando spectroscopies. *Chem Catalysis* **2022**, *2* (9), 2312-2327. <https://doi.org/10.1016/j.checat.2022.07.016>.
- 93 Park, Y. S.; Lee, J. H.; Jang, M. J.; Jeong, J.; Park, S. M.; Choi, W.-S.; Kim, Y.; Yang, J.; Choi, S. M. Co₃S₄ nanosheets on Ni foam via electrodeposition with sulfurization as highly active electrocatalysts for anion exchange membrane electrolyzer. *International Journal of Hydrogen Energy* **2019**, *45* (1), 36-45. <https://doi.org/10.1016/j.ijhydene.2019.10.169>.
- 94 Wang, X.; Lammertink, R. G. H. Dimensionally stable multication-crosslinked poly(arylene piperidinium) membranes for water electrolysis. *Journal of Materials Chemistry A* **2022**, *10* (15), 8401-8412. <https://doi.org/10.1039/d1ta10820d>.
- 95 Wang, M. H.; Lou, Z. X.; Wu, X.; Liu, Y.; Zhao, J. Y.; Sun, K. Z.; Li, W. X.; Chen, J.; Yuan, H. Y.; Zhu, M.; Dai, S.; Liu, P. F.; Yang, H. G. Operando high-valence Cr-modified NiFe hydroxides for water oxidation. *Small* **2022**, *18* (19), 2200303. <https://doi.org/10.1002/sml.202200303>.

Chapter 4

Self-supported Cu/Co-based Nanoheterostructures for High-efficiency Alcohol Oxidation and Hydrogen Production



The results presented in this chapter have been published in *Advanced Science* as “*Microwave-assisted synthesis of Cu/Co-based nanoheterostructures for high-efficiency alcohol oxidation*” by Xuesong Zhang, Jaume Gázquez, Arturo Pajares, Dino Tonti, and Pablo Guardia (<https://doi.org/10.1002/advs.202505581>). The text and figures have been adapted for the purpose of this thesis: the introduction was slightly revised, and some figures were re-edited for consistency with the thesis format. In addition, Section 4.3.5 contains new experimental results that were not included in the publication.

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Chapter Summary

Hybrid water splitting, using methanol or ethanol oxidation reactions (MOR and EOR) at the counter electrode during electrochemical hydrogen generation, offers an efficient alternative to the sluggish oxygen evolution reaction (OER) by delivering lower overpotential and faster reaction kinetics. Herein, we report Cu/Co-based core-shell nanocrystals (NCs) showing excellent performance for both MOR and EOR. The structure, composition, and size of the NCs can be controlled by adjusting the synthesis parameters in a one-pot microwave (MW)-assisted process. The electrocatalytic performance of the NCs shows lower potentials for both MOR and EOR (155 and 197 mV at $50 \text{ mA}\cdot\text{cm}^{-2}$, respectively) compared to the OER. They consist of a copper-rich metallic core initially encapsulated by a shell composed of cobalt oxide and cobalt carbide. This nanoheterostructure evolves to a copper oxide core surrounded by an oxide shell consisting of small cobalt- and copper-oxide nanodomains upon chronopotentiometry experiments. The excellent performance in both MOR and EOR is attributed to the oxidation of the NCs and a concomitant diffusion process that forms small oxide clusters. The final structure provided NCs with high mass activities for both alcohol oxidation reactions, producing formic and acetic acid as products (for MOR and EOR, respectively). Finally, the NCs were tested for hybrid water electrolysis, demonstrating high hydrogen production along with high stability. In particular, the performance of the NCs was kept constant for over 60 hours at different current densities (10 to $50 \text{ mA}\cdot\text{cm}^{-2}$).

4.1 Introduction

Even though electrochemical water splitting is widely acknowledged as one of the most environmentally friendly processes to produce green hydrogen, especially when powered by renewable energy sources.^{1,2} Nevertheless, the multiple electron transfer for the oxygen evolution reaction (OER) at the anode leads to a large energy barrier, which limits the kinetics of the overall splitting of water.^{3,4} To circumvent this issue, the sluggish OER can be replaced by a thermodynamically more favorable oxidation reaction, the so-called hybrid water electrolysis,^{5,6} as we mentioned in **Section 1.3.3**.

Molecules such as alcohols, amines, urea, hydrazine, or carbohydrates have been studied intensively as excellent candidates for the cost-efficient and environmentally friendly production of hydrogen.^{7–9} Among them, methanol and ethanol stand out as excellent fuels for hybrid water electrolysis and direct alcohol fuel cells due to their high energy densities (17.3 and 22.7 MJ·L⁻¹, respectively), ease of fuel handling, and low cost.^{10,11} Both methanol and ethanol oxidation reactions (MOR and EOR, respectively) have been extensively studied to identify oxidation pathways that can lead to the total or partial oxidation of alcohol. While complete oxidation of both alcohols delivers the highest current densities (6 and 12 electrons for MOR and EOR, respectively), it also produces CO₂, which increases the carbon footprint of the overall hydrogen production. In contrast, the partial oxidation of methanol or ethanol allows for the concomitant production of hydrogen and value-added molecules under a zero-carbon footprint. In particular, formic acid follows the CO-free oxidation pathway in the MOR, and acetic acid follows the C₂ pathway in the EOR.¹² The reaction pathways have been demonstrated by Eq. (8, and 12-15) in **Section 1.3.3**. In this context, ethanol emerges as a superior candidate for sustainable hydrogen production compared to methanol, owing to its higher energy density, lower toxicity, and renewable production from biomass.¹³

During hybrid water splitting, the applied voltages must remain below the required for the OER, thereby constraining the operating current densities and subsequently reducing the overall electrochemical efficiency.^{14,15} This reduction in the current density is largely offset by the simultaneous production of hydrogen and value-added molecules with zero CO₂ emissions. For instance, by exploiting the electro-oxidation of organic compounds, Yu et al. reduced the energy costs in about 14.3%.¹⁶

Nevertheless, the electrocatalytic performance still requires improvements to achieve industrially viable Faradaic efficiencies and to attain current densities at a moderate applied potential. For the MOR, but particularly for the EOR, this is achieved by noble metal- (Pt- or Pd-) and nickel-based catalysts, which raises additional environmental and economic concerns.^{17–19} For instance, Qin et al. synthesized PtRuNiCoFeGaPbW high entropy alloy ultrathin nanowires to oxidate methanol to CO₂.²⁰ In these circumstances, transition metal-based NCs (Cu, Co, and Ni) have been identified as potential electrocatalysts for alcohol oxidation reactions, offering an environmentally friendly and economically sustainable hydrogen production.²¹ For instance, Cu-based materials show a high affinity to adsorb methanol, and hence, high activity for the MOR on Cu-based NCs has been reported.²² Simultaneously, cobalt-based catalysts have attracted much attention for their excellent performance in water splitting, in particular for the OER and MOR.^{18,23,24} Interestingly, cobalt doping in Ni-, Pt- and Pd-based catalysts results in an enhancement of the catalytic activity.^{25,26}

The combination of copper and cobalt in a NC has garnered significant attention due to the enhancement of the catalytic activity. Recently, various Cu-Co nanomaterials, such as Cu@CoO_x,²⁷ CuCo₂O₄,²⁸ copper cobalt phosphides,²⁹ copper cobalt selenide,³⁰ copper cobalt layered double hydroxide,³¹ boron-copper cobalt oxides,³² copper cobalt hydroxycarbonates,³³ or copper cobalt sulfide,³⁴ have been reported.

The formation of Mott-Schottky heterostructures has shown promising results in improving the intrinsic conductivity of oxide semiconductors.³⁵ This approach induces interface effects in catalysts, such as electronic coupling, charge transfer, and defects, and optimizes the heterostructure's intermediate adsorption/desorption behavior.³⁶ The increased active site availability results in a superior electrocatalytic performance. Moreover, exploiting the Mott-Schottky heterojunction interface between metal and semiconductor can significantly enhance semiconductor Fermi level management, utilizing Schottky barriers to achieve rectifying effects and confining semiconductor hole or electron states, thereby significantly improving electrocatalytic performance.³⁷ Additionally, transition metal carbides are potential alternatives to platinum-based catalysts, leveraging their platinum-like electronic structures. Furthermore, synthesizing highly dispersed carbides as core nanoparticles supports synergistic enhancements.³⁸ Recent literature underscores that synthesizing Mott-Schottky heterostructures typically involves multistep syntheses, rendering them complex and

time-consuming.^{36,39-41} Hence, there is an urgent need to explore a more rapid and streamlined synthesis route.

In this work, we report a one-pot microwave (MW)-assisted synthesis for producing Cu/Co-based nanoheterostructures. These heterostructures, consisting of a metal core surrounded by a metal-oxide/metal-carbide shell, are embedded or self-supported on a metal-oxide sheet. Adjusting the feeding molar ratio between the copper and cobalt precursors provides control over the compositions of the core-shell NCs and the morphology of supporting metal-oxide nanosheets. For instance, an excess of cobalt precursor leads to the formation of a CuCo alloy at the core and cobalt carbide and cobalt oxide domains at the shell. Under an applied potential, the structure evolves due to the diffusion and partial oxidation of atoms, resulting in an oxidized core surrounded by small Cu- and Co-oxide domains. This process boosts the formation of Mott-Schottky heterojunctions along the structure, providing high electrocatalytic performance for both MOR and EOR. The nanoheterostructures were tested for hybrid water splitting, showing high stability under moderate current densities and the production of value-added products such as formic or acetic acid.

4.2 Experimental

This section describes the details of the chemicals used in the reaction, synthesis process, ligand removal, characterization techniques, and electrochemical measurements.

4.2.1 Materials

Cobalt(II) acetylacetonate ($\text{Co}(\text{acac})_2$, $\geq 99.9\%$), copper(II) acetylacetonate ($\text{Cu}(\text{acac})_2$, $\geq 99.9\%$), benzyl alcohol (for synthesis), nafion 117 containing solution ($\sim 5\%$ in a mixture of low aliphatic) and 2-propanol ($\geq 99.5\%$) were purchased from Sigma-Aldrich. Polyvinylpyrrolidone ($\text{PVP}_{3.5\text{k}}$, $M_w = 3,500$) and potassium hydroxide (KOH , 85% ACS reagent) were purchased from Thermo Fisher Scientific. Carbon black (Vulcan CX-72) was purchased from FuelCellStore. All materials were used as received without further purification. Milli-Q water ($18.2 \text{ M}\Omega \cdot \text{cm}$, Milli-Q H_2O , Merck Millipore) was used for all the experiments and solutions. Pt/C catalyst (20 wt% of Pt loading) was purchased from Quintech. Carbon cloth (W0S1101) was purchased from CeTech Co., Ltd.

4.2.2 MW-assisted Synthesis of Cu/Co NCs

For the MW-assisted synthesis of Cu/Co NCs, a MW reactor (CEM Discover SP) operating at a frequency of 2.45 GHz and a power of 300 W was used. The reaction process is shown in [Figure 4.1](#).

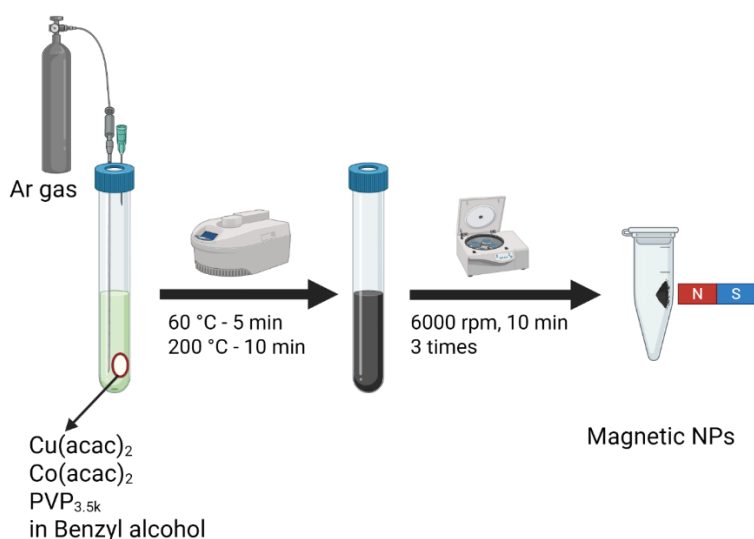


Figure 4.1 Schematic diagram of MW-assisted synthesis of Cu/Co NCs

Samples were produced by modifying a procedure for the synthesis of Cu₂O NCs previously reported by our group.⁴² The amount of benzyl alcohol and PVP_{3.5k} were kept constant to 4 mL and 136 mg (0.038 mmol), respectively. The copper to cobalt molar feeding ratio was modified keeping a final metal concentration of 17.5 mM (Co + Cu). For instance, for a 2:1 copper to cobalt ratio, 136 mg of PVP_{3.5k} (0.038 mmol) were dissolved in 4 ml of benzyl alcohol through continuous sonication (20 minutes) in a 10 mL reaction tube. Next, 12.30 mg of Cu(acac)₂ (0.047 mmol) and 5.90 mg of Co(acac)₂ (0.023 mmol) were added into the reaction tube, and the solution was sonicated further until a homogeneous solution was formed (ca. 30 minutes). The final solution was then purged by bubbling with an Ar flow for at least 20 minutes and the tube was sealed with a rubber. Finally, the tube was placed inside the MW reactor, heated to 60 °C, and kept at that temperature for 5 minutes. The temperature was then raised up to 200 °C (ca. 180 seconds) and kept at 200 °C for 10 minutes before cooling down to room temperature with compressed air. The NCs were collected by adding 30 ml of acetone followed by centrifugation at 6000 rpm for 10 minutes. The supernatant was discarded and the procedure repeated at least 3 times before drying the precipitate under vacuum at room temperature. Based on the copper-to-cobalt molar ratio, the sample was labelled as CuCo_{2/1}.

Samples with different copper to cobalt molar ratios were synthesized following the same procedure but adjusting the feeding Cu(acac)₂ and Co(acac)₂ ratios. In detail, the copper: cobalt feeding molar ratio was adjusted to 1:4, 1:2, 1:1 and 4:1 leading to the synthesis of the CuCo_{1/4}, CuCo_{1/2}, CuCo_{1/1}, CuCo_{2/1}, CuCo_{4/1} samples, respectively. Additionally, control samples using only Cu(acac)₂ or Co(acac)₂ (1:0 or 0:1 molar ratio) were synthesized. These samples were labeled as Cu₂O (CuCo_{1/0}) and CoO (CuCo_{0/1}), respectively.

4.2.3 NCs Characterization

X-ray Diffraction (XRD)

Patterns were collected using a conventional Cu-K α radiation source ($\lambda = 1.5406 \text{ \AA}$) in a Bruker ADVANCE D8 employing a Bragg-Brentano geometry. Intensity was recorded within the 2θ range from 20 to 80° at a scanning step of $0.02^\circ \cdot \text{s}^{-1}$. Samples were

prepared by drop-casting and further evaporating a concentrated solution of NCs onto an amorphous silicon wafer.

TEM and HR-TEM analysis

Low-resolution electron micrographs were obtained using a JEOL 1210 transmission electron microscope operating at 120 kV, equipped with a side-entry 60°/30° double tilt GATAN 646 specimen holder. For high-resolution TEM (HR-TEM) and high-angle annular dark-field scanning TEM (HAADF-STEM) images as well as electron energy loss spectroscopy (EELS) mapping a FEI Titan microscope operated at 300 kV were used. Samples were prepared by drop-casting a diluted solution of NCs onto carbon-coated Au- or lacy carbon Cu-grids (400 mesh).

X-ray Photoelectron Spectroscopy (XPS)

XPS measurements were done in a SPECS PHOIBOS 150 hemispherical energy analyzer using Al K α X-ray radiation (1486.6 eV) for excitation.

Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-OES)

To determine the final copper to cobalt ratio in the NCs, as well as the yield of the reaction, ICP-OES was carried out using an Agilent model 5900. Samples were prepared by digesting ~1 mg of NCs in 1 ml of aqua regia for 30 minutes. The solution was diluted with Milli-Q water reaching a final volume of 10 mL.

4.2.4 Electrochemical Characterization

The electrochemical performance of each sample was analyzed utilizing a Bio-logic VMP3 multichannel potentiostat. A conventional three-electrode configuration was employed where a 5 mm diameter glassy carbon disk was used as the working electrode (WE), a platinum mesh as the counter electrode (CE) and a Hg/HgO electrode as the reference electrode (RE). Cyclic voltammetry (CV) in 1 M KOH at a sweeping rate of 50 mV·s⁻¹ were performed for each catalyst.

Preparation of the Catalysts

The produced NCs were supported onto carbon black to prepare the catalyst and evaluate their electrocatalytic activity. In detail, 4 mg of Cu/Co NCs and 2 mg of carbon black (2:1, mass ratio) were dispersed in 5 mL of ethanol through continuous sonication for 3 hours to ensure a homogenous mixing. The suspension was then dried under vacuum at 60 °C for 6 h. Finally, 5 mg of the dried catalyst was dispersed in a 1 mL of solution (200 μ L of Milli-Q water, 700 μ L of 2-propanol and 100 μ L of Nafion) and sonicated for 30 minutes until a homogenous ink was formed.

Preparation of the WE

First, the surface of the electrode was polished with alumina powder until achieving a mirror-like surface. Afterwards, 5 μ L of the catalyst ink containing the Cu/Co NCs was drop-casted onto the WE surface. All potentials were corrected to the reversible hydrogen electrode (RHE) according to the following equation: $E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.059 \cdot \text{pH} + 0.098 \text{ V}$, where the pH was determined by a pH meter.

OER, MOR and EOR Characterization

For evaluating the performance of the samples for OER, MOR and EOR, CV curves were acquired in a KOH solution containing different concentrations of methanol or ethanol (0, 0.5, 1, 2, and 4 M). Tafel slopes were determined from Tafel plots following the equation: $\eta = b \cdot \log j + c$, where b is the Tafel slope, η is the overpotential and j is the current density. Electrochemical double-layer capacitance (C_{dl}) curves were measured by running CV curves in the non-Faradaic region (1.174- 1.274 V vs. RHE) at different scan rates (from 20 to 100 $\text{mV} \cdot \text{s}^{-1}$). The C_{dl} was calculated by following the equation: $C_{\text{dl}} = \Delta j / v$, where $\Delta j = (j_{\text{a}} - j_{\text{c}}) / 2$ is the current density (at 1.224 V vs. RHE, $\text{mA} \cdot \text{cm}^{-2}$) and v is the scan rate ($\text{mV} \cdot \text{s}^{-1}$). The electrochemical active surface area (ECSA) was calculated as: $\text{ECSA} = C_{\text{dl}} / C_{\text{s}}$, where a general specific capacitance (C_{s}) of $0.04 \text{ mF} \cdot \text{cm}^{-2}$ in 1 M KOH was used.⁴³ Electrochemical impedance spectroscopy (EIS) was acquired with an amplitude of 5 mV at frequencies ranging from 10^6 to 10^{-2} Hz. Finally, the mass activity (MA) of the catalyst was calculated according to the following equations: $\text{MA} = j / m$, where j is the measured current density ($\text{mA} \cdot \text{cm}^{-2}$) and m is the mass of NCs. Partial iR compensation (90%) was applied to all data manually.

Hydrogen Production

Standard and hybrid water electrolysis were evaluated using a two-electrode configuration employing a HCl-activated carbon cloth (CC) ($1 \times 1.5 \text{ cm}^2$, working area is $1 \times 1 \text{ cm}^2$) as both anode and cathode.

Electrodes were prepared by drop-casting a solution containing $\text{CuCo}_{2/1}$ NCs (anode) or Pt/C (cathode). For instance, 5 mg of $\text{CuCo}_{2/1}$ NCs were dispersed in a solution containing 200 μL of MQ- H_2O , 700 μL of 2-propanol and 100 μL of Nafion under 3 h of sonication. Next, 200 μL of this solution were drop casted onto the CC to achieve a loading of $1 \text{ mg}\cdot\text{cm}^{-2}$. The anode was labeled as $\text{CuCo}_{2/1}/\text{CC}$. The same procedure was used to prepare the cathode but replacing the $\text{CuCo}_{2/1}$ NCs by commercial Pt/C. In this particular case, 400 μL were drop casted onto the CC to achieve $2 \text{ mg}\cdot\text{cm}^{-2}$ (anode labeled as Pt/C/CC).

Linear sweep voltammetry (LSV) was applied to both anodes in a 1 M KOH electrolyte solution (standard water splitting) and in a 1 M KOH electrolyte solution containing 1 M methanol and ethanol concentrations (hybrid water-splitting). Data were analyzed using the same equations described previously. Stability tests were carried out by running chronopotentiometry measurements at 10, 20, 30, 40, 50 $\text{mA}\cdot\text{cm}^{-2}$ for 60 hours for both methanol and ethanol hybrid water splitting.

4.2.5 Fabrication and Operation of An Anion Exchange Membrane Hybrid Alcohol Electrolyzer Single Cells

Membrane electrode assemblies (MEAs) with 1.0 cm^2 active area were prepared by sandwiching a Nafion 117 membrane between the $\text{CuCo}_{2/1}$ anode and the drop-cast Pt/C cathode ($\text{CuCo}_{2/1}||\text{Pt/C}$). For comparison, a RuO_2 anode was used, resulting in a $\text{RuO}_2||\text{Pt/C}$ sandwich structure.

Electrolyte circulation (1 M KOH or 1 M KOH with 1 M methanol/ethanol) was maintained at $1.0 \text{ mL}\cdot\text{s}^{-1}$ through the anode and cathode compartments via peristaltic pumps. Before testing, MEAs were activated by CV at $100 \text{ mV}\cdot\text{s}^{-1}$ for 60 cycles.

Polarization curves were acquired via LSV at $5 \text{ mV}\cdot\text{s}^{-1}$ with three independent measurements for statistical reliability.

4.2.6 Characterization of the Hybrid Water Splitting Products

To characterize the byproducts of the hybrid methanol or ethanol electrolysis, the electrolyte was analyzed after chronopotentiometry measurements at $40 \text{ mA} \cdot \text{cm}^{-2}$ over time (0, 3, 6, 12 hours) in a H-type cell employing Nafion 117 membrane. In detail, 0.3 mL of the electrolyte was mixed with 0.3 mL of D_2O and ^{13}C and ^1H nuclear magnetic resonance (NMR) spectroscopies were carried out in a Bruker Avance III™ HD 400 MHz. For a quantitative analysis, maleic acid (0.1 mL) was used as an internal standard.⁴⁴ The corresponding selectivity (S) and faradaic efficiencies (FE) for each reaction were calculated at a static current at different times by using the following equations:

$$S(\%) = \frac{N}{N_{OH}} \cdot 100; \quad FE(\%) = \frac{\sum N_i \cdot 4F}{Q} \cdot 100$$

Where N is the moles of the as-produced molecule, N_{OH} is the moles of consumed alcohol (methanol or ethanol), Q is the total charge passed through the system recorded during electrolysis and F is the Faradaic constant ($96485 \text{ C} \cdot \text{mol}^{-1}$).

4.3 Results and Discussion

The characterization of NCs and electrochemical measurements for OER, MOR, and EOR is discussed in detail below.

4.3.1 Synthesis and Characterization of Cu/Co NCs

Self-supported Cu/Co NCs were produced by a novel MW-assisted synthesis route developed in this work. In particular, different molar ratios of copper- and cobalt-acetylacetonates (*i.e.* Cu:Co ranging from 1:4 to 4:1) were mixed in benzyl alcohol containing PVP_{3.5k}. In all the experiments, the total metal concentration in solution was kept constant at 17.5 mM. After MW radiation, nanoheterostructures consisting of NCs (regions with higher electron density) formed on top of thin substrates (areas of lower electron density) were observed ([Figure 4.2](#)). Despite these nanoheterostructures varied in size according to the Cu:Co ratio, we could not identify a clear trend allowing for a precise size control. Nevertheless, nanoheterostructures produced at 1:4 and 4:1 molar ratios show the larger cores ([Figure 4.2a](#) and [e](#), respectively). According to

the XRD results, all samples showed peaks consistent with the Fm-3m(225) structure of a $\text{Cu}_{0.48}\text{Co}_{0.52}$ alloy (JCPDS #50-1452). However, for the [111] and [200] peaks, we observed a deviation that was accentuated, in particular, for $\text{CuCo}_{1/4}$ and $\text{CuCo}_{1/2}$ samples, with peaks shifting toward higher angles as cobalt content increased ([Figure 4.3](#)). This is consistent with the differences between the [111] peak of copper (43.297° [111], JCPDS #04-0836) and cobalt (44.216° [111], JCPDS #15-0806). Additionally, the presence of a broad peak at around 61° and a small peak at 41.5° for the $\text{CuCo}_{1/4}$ sample suggested the presence of copper or cobalt oxides. These results are compatible with the formation of a metallic Cu_xCo_y core, self-supported by a copper- and/or cobalt oxide shell.

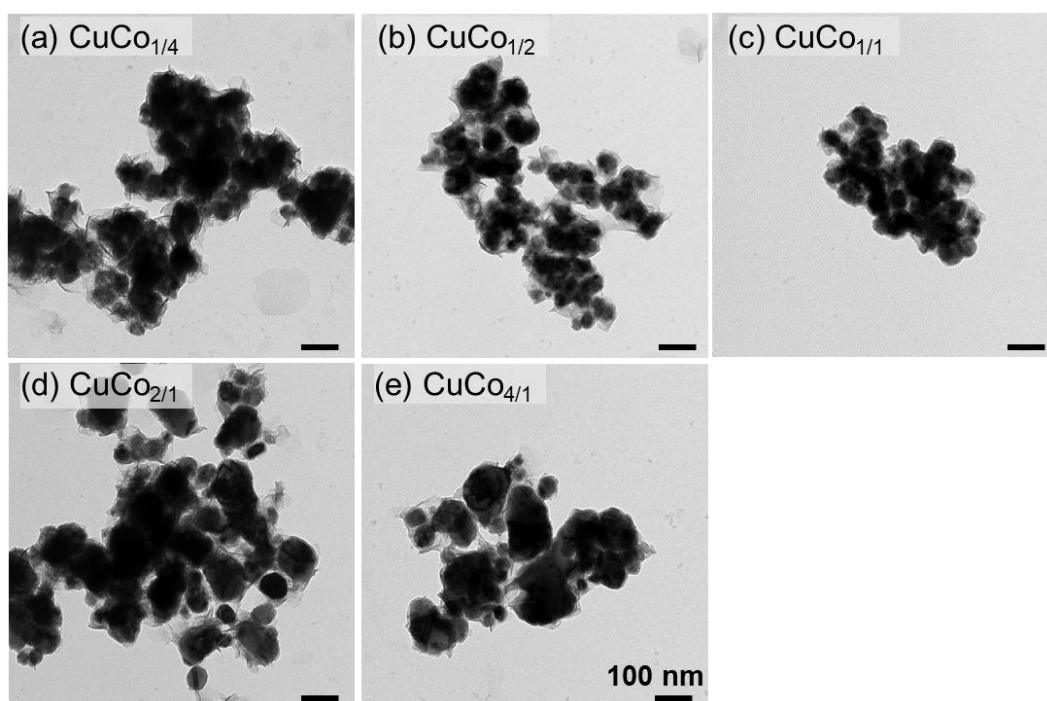


Figure 4.2 TEM images of Cu/Co NCs produced by a MW-assisted route at 200°C adding different Cu:Co feeding molar ratios: (a) 1:4 - $\text{CuCo}_{1/4}$, (b) 1:2 - $\text{CuCo}_{1/2}$, (c) 1:1 - $\text{CuCo}_{1/1}$, (d) 2:1 - $\text{CuCo}_{2/1}$, (e) 4:1 - $\text{CuCo}_{4/1}$. All the scale bars correspond to 100 nm

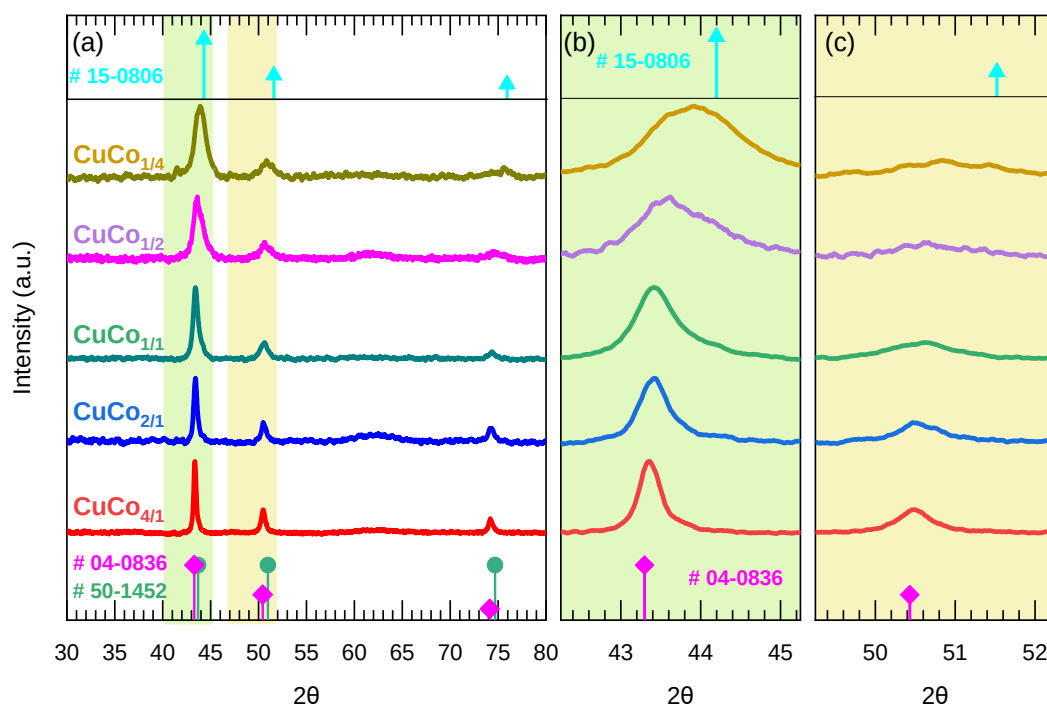


Figure 4.3 XRD patterns of Cu/Co NCs along with the reference for $\text{Cu}_{0.48}\text{Co}_{0.52}$ alloy (JCPDS: #50-1452) and the enlarged XRD pattern.

According to the literature, the formation of a metallic core was unexpected, as similar conditions led to the formation of metal oxides.⁴² Control experiments were carried out by adding only one of the metal precursors ($\text{Cu}(\text{acac})_2$ or $\text{Co}(\text{acac})_2$ at ratios of 1:0 and 0:1, respectively), leading to the formation of Cu_2O and CoO NCs ([Figure 4.4](#)). This observation indicates that neither the $\text{PVP}_{3.5\text{k}}$, benzyl alcohol, nor the purging of the tube with argon, did provide enough reductive conditions to produce metallic NCs. Nonetheless, it is worth noticing that the synthesis conditions promote the reduction of copper precursor from Cu^{2+} to Cu^+ , resulting in the formation of a Cu_2O phase. Thus, the formation of a metallic core would result from a redox synergy reaction between copper and cobalt complexes under these conditions as has been reported for instance for CuNi NCs.⁴⁵ Further characterization confirmed that a Cu-rich metallic core is formed in all the samples while cobalt is distributed between the core and the shell (see discussion below).

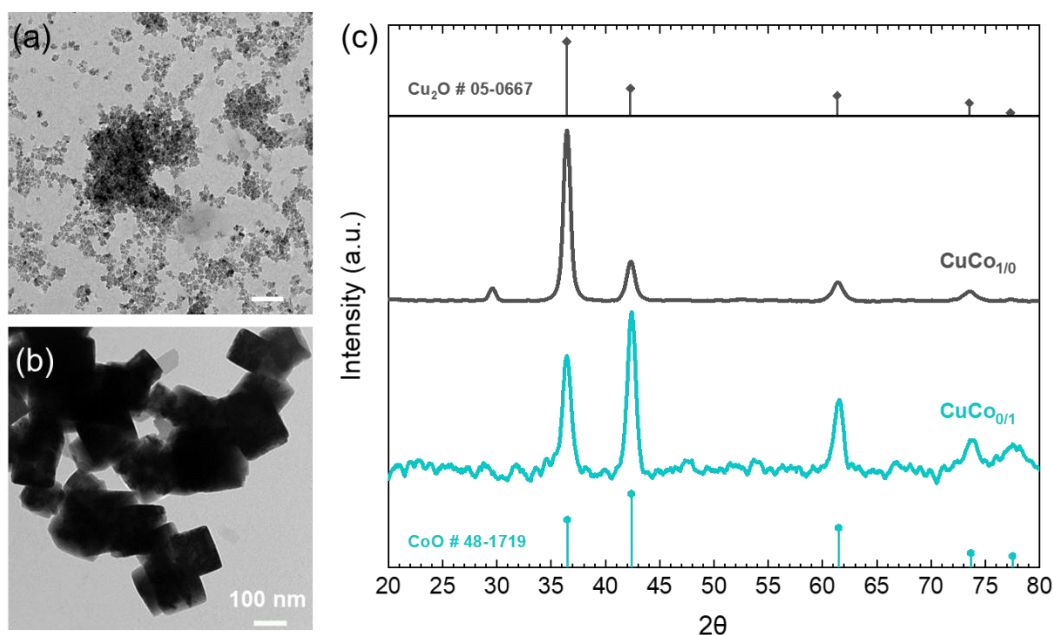


Figure 4.4 TEM images of a) 1:0 - CoO ($\text{CuCo}_{0/1}$), b) 0:1 - Cu_2O ($\text{CuCo}_{1/0}$) produced by a microwave-assisted route at 200 °C. All the scale bars are corresponding to 100 nm. (c) XRD patterns of (a, b).

To further understand the formation of the Cu/Co NCs, the final stoichiometry of the samples was analyzed by ICP-OES ([Figure 4.5](#)). According to the results, we systematically observed a slightly higher copper content compared to the initial Cu:Co feeding ratios. For instance, the final copper contents for $\text{CuCo}_{1/4}$ (20.0%), $\text{CuCo}_{1/2}$ (33.3%), $\text{CuCo}_{1/1}$ (50.0%), $\text{CuCo}_{2/1}$ (66.6%) and $\text{CuCo}_{4/1}$ (80.0%) were 23.1, 36.2, 55.8, 71.3 and 82.0%, respectively.

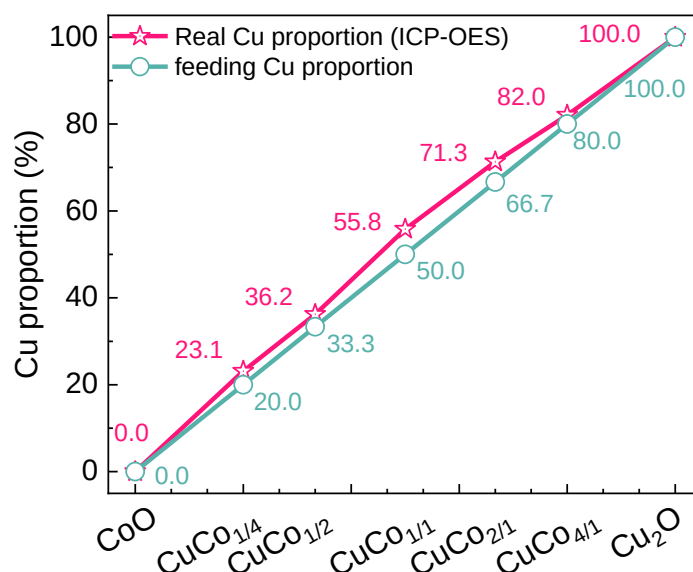


Figure 4.5 The comparison between feeding Cu and real Cu content determined by ICP-OES.

4.3.2 Electrocatalytic Characterization of Cu/Co NCs

The electrocatalytic performances of the Cu/Co NCs for the OER, MOR, and EOR were evaluated at room temperature using a conventional three-electrode system. Samples produced at 0:1 and 1:0 ratios (labeled as CoO and Cu₂O, respectively) were also tested for a consistent analysis. All the measurements were carried out in a 1 M KOH electrolyte (OER), with additional methanol or ethanol (0.5 M) added for the MOR and EOR, respectively (see experimental section for details). The summary of the CV polarization curves along with Tafel and C_{dl} plots are reported in [Figure 4.6](#), [4.7](#), [4.8](#).

Cu/Co NCs Performance for the OER

Cu₂O and CoO samples show the lowest OER activity among all samples ([Figure 4.6](#)). In particular, the Cu₂O exhibited an onset potential above 1.60 V and overpotential of 470 mV (applied potential: 1.70 V) at 10 mA·cm⁻², with the highest Tafel slope (136 mV·dec⁻¹) and the lowest C_{dl} value (3.02 mF·cm⁻²). This performance obtained for the copper oxide NCs is consistent with previously published studies.⁴⁶ CoO NCs' performance slightly improves with a lower overpotential (1.60 V vs. RHE, overpotential of 370 mV) at 10 mA·cm⁻² and Tafel slope (79 mV·dec⁻¹). Yet, those values were still high compared to the substantial improvement in OER activity

observed for Cu/Co NCs prepared with both copper and cobalt, where curves practically overlap for all samples. A closer look revealed that the Cu/Co nanoheterostructures produced at the highest cobalt contents showed the best performances (CuCo_{1/4} and CuCo_{1/2}), with CuCo_{1/2} achieving the lowest overpotentials (overpotentials of 310 and 390 mV at 10 and 50 mA·cm⁻², respectively). For comparison, the CuCo_{2/1} sample showed slightly higher overpotentials (overpotential of 340 and 410 mV at 10 and 50 mA·cm⁻², respectively). This suggests that increasing cobalt content enhances the OER efficiency, which is in good agreement with the superior OER performance of CoO relative to Cu₂O alone. Despite the significant improvement of the Cu/Co NCs compared to the metal-oxide NCs, these values remain comparable to those thus far reported in the literature for similar bimetallic nanoparticles.^{47,48}

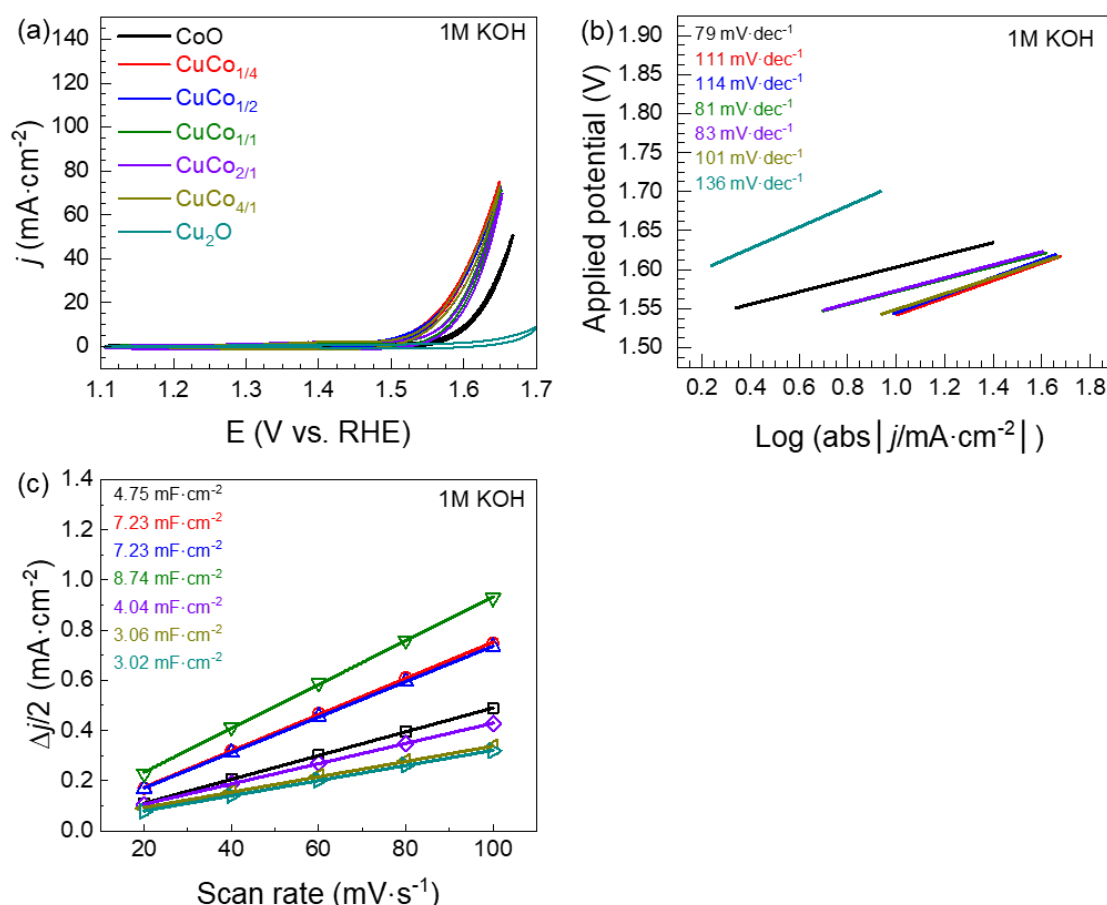


Figure 4.6 OER performance: (a) CV curves, (b) Tafel, and (c) C_{dl} plots for all Cu/Co NCs samples measured in 1 M KOH. All potentials were corrected to the RHE, and 90% of iR compensation.

Cu/Co NCs Performance for the MOR

The addition of methanol to the electrolyte (0.5 M) resulted in a significant modification of the polarization curves ([Figure 4.7a-c](#)). On one hand, the presence of methanol clearly improved the activity for the Cu₂O NCs, displaying an onset potential at 1.46 V, an applied potential of 1.50 V at 10 mA·cm⁻², and a reduced Tafel slope (101 mV·dec⁻¹). Conversely, CoO NCs showed lower performance in the presence of methanol, as evidenced by higher overpotentials and steeper Tafel slopes than those measured for the OER. On the other hand, also in this case in all the Cu/Co NCs the performances improved with respect to the metal-oxide NCs, exhibiting lower onset potentials (below 1.40 V vs. RHE) and lower required potentials, along with a notable oxidation peak observed at approximately 1.54 V vs. RHE, characteristic of the occurrence of the MOR. According to the CV curves, activity increased with the increasing amount of copper in the NCs, reaching a peak performance for the CuCo_{2/1} sample. This sample showed the lowest applied potentials (1.42 and 1.48 V at 10 and 50 mA·cm⁻², respectively) and lower Tafel slope (76 mV·dec⁻¹), along with the highest oxidation peak current density (81.45 mA·cm⁻² at 1.55 V vs. RHE) and the largest ECSA (277.75 cm²·mg⁻¹). This trend was opposite to the one observed for the OER, where performances improved with increasing content of Co. Remarkably, the CuCo_{1/1} sample showed similar performance as the CuCo_{2/1} at lower potentials, though its performance decay as the potential increases, delivering lower current densities (1.42 and 1.51 V vs. RHE at 10 and 50 mA·cm⁻², respectively, [Figure 4.7a](#)).

Following the preliminary analysis, we studied the effect of the methanol concentration on the electrocatalytic performance of the CuCo_{2/1} NCs. CV curves were recorded at different methanol concentrations (0, 0.5, 1, 2, 4 M, [Figure 4.7d](#)). Results showed a significant decrease in onset potential as the methanol concentration increased. At the same time, the oxidation peak at around 1.54 V vs. RHE gradually vanished, shifting from 1.55 to 1.40 V vs. RHE. This observation clearly indicates an optimal methanol concentration for our experimental set-up, where a trade-off between the oxidation and diffusion rates is accomplished at the WE interface. At low concentrations, the reaction kinetics is likely limited by the diffusion of methanol molecules to the electrode surface. Instead, at higher concentrations, the methanol concentration and the oxidation products likely saturate the electrode's surface, thus decreasing the activity and, hence, the intensity of the oxidation peak.

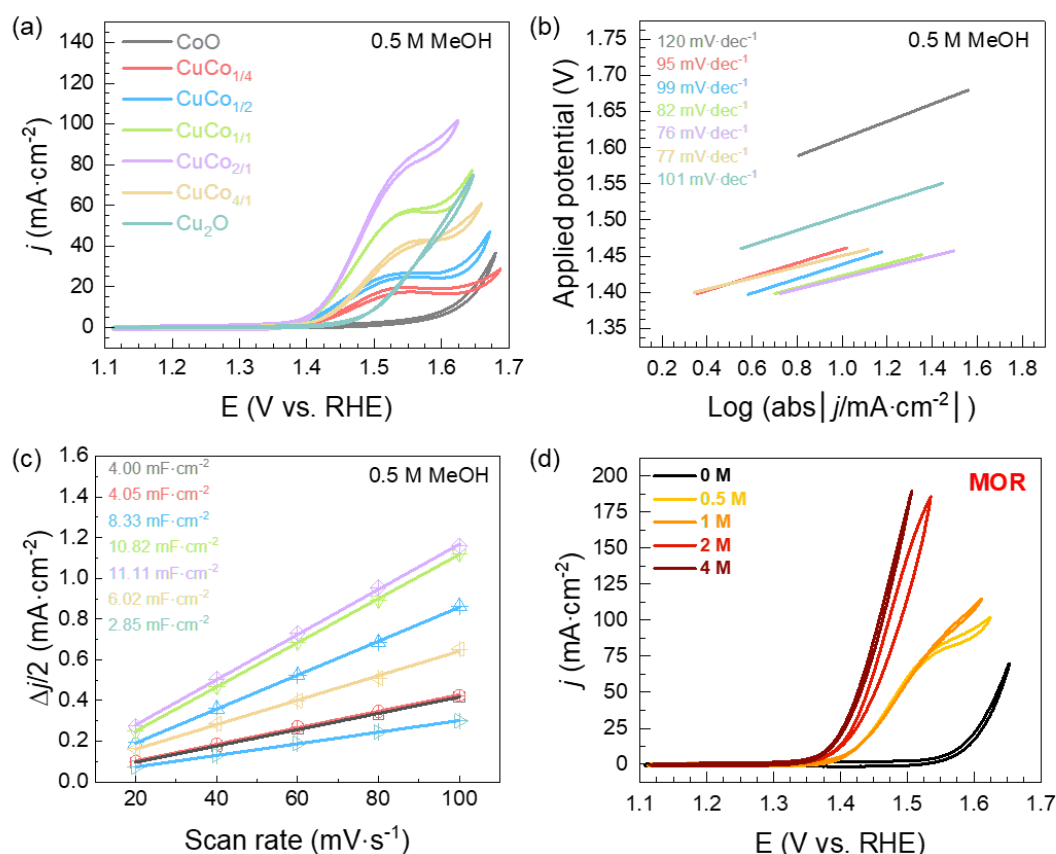


Figure 4.7 MOR performance: (a) CV curves, (b) Tafel, and (c) C_{dl} plots for all Cu/Co NCs samples measured in 1 M KOH with 0.5 M methanol. (d) CV curves of CuCo_{2/1} at different methanol concentrations (0, 0.5, 1, 2, 4 M). All potentials were corrected to the RHE, and 90% of iR compensation.

Cu/Co NCs Performance for the EOR

Finally, samples were tested for the EOR by adding 0.5 M ethanol into the electrolyte, as shown in [Figure 4.8](#). Compared to methanol, ethanol is a non-toxic compound that can be produced from biomass or agriculture feedstocks as well as waste. However, it has been well-established that the presence of a higher carbon content results in lower oxidation efficiency.¹⁷ Indeed, we observed higher potentials at 10 mA·cm⁻² for both oxides during the EOR (1.52 and 1.63 V at 10 mA·cm⁻² for Cu₂O and CoO, respectively) compared to the ones for MOR (1.46 and 1.61 V at 10 mA·cm⁻² for Cu₂O and CoO, respectively). Certainly, this difference was particularly pronounced in the Cu₂O sample, which exhibited higher values than the CoO. This indicates that cobalt demonstrates superior performance compared to copper, in contrast with the better performance of Cu₂O for the MOR.

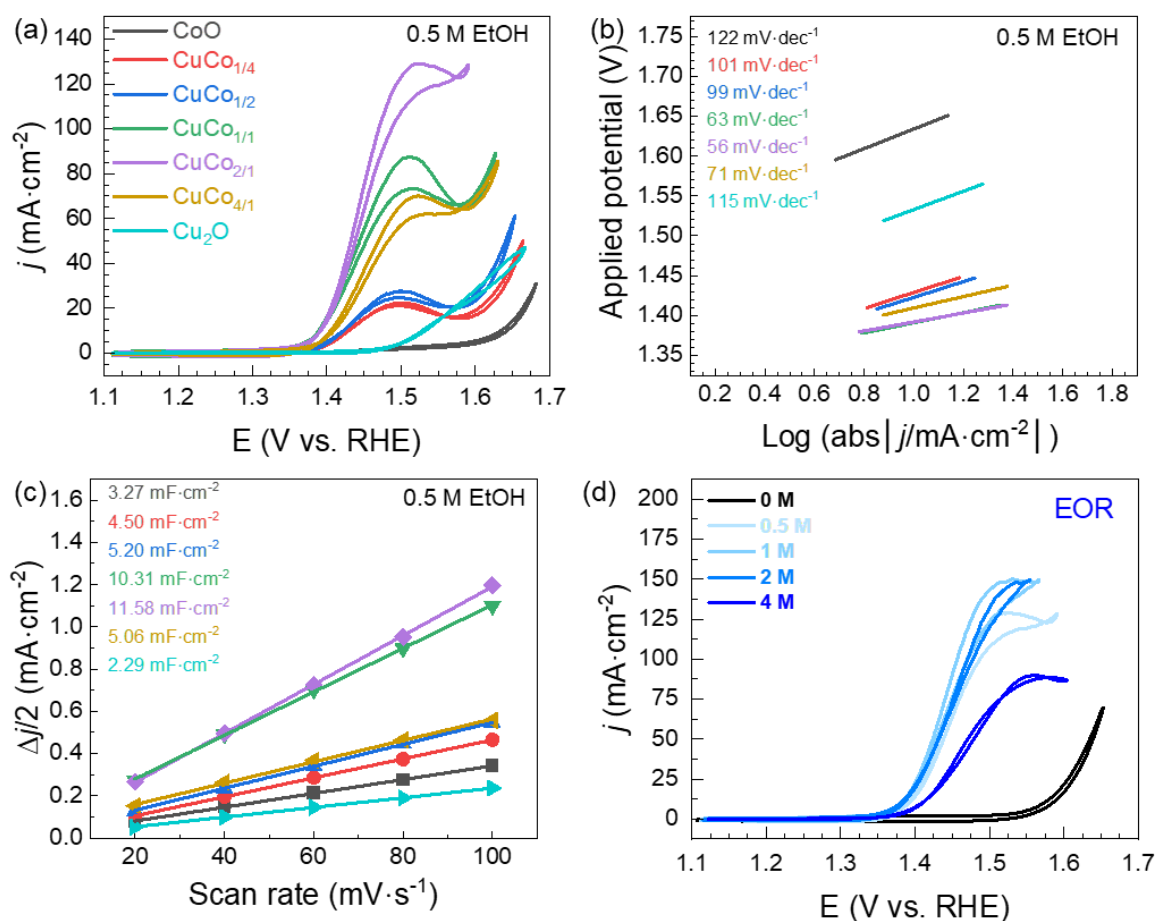


Figure 4.8 EOR performance: (a) CV curves, (b) Tafel, and (c) C_{dl} plots for all Cu/Co NCs samples measured in 1 M KOH with 0.5 M ethanol. (d) CV curves of CuCo_{2/1} at different ethanol concentrations (0, 0.5, 1, 2, 4 M). All potentials were corrected to the RHE, and 90% of iR compensation.

When analyzing the EOR activity of the Cu/Co NCs, all samples exhibited lower onset potentials compared to Cu₂O and CoO, reflecting a similar trend to that observed for the MOR. The electrooxidation activity increased as the content of copper in the NCs increased, reaching its maximum for CuCo_{2/1} NCs. In particular, this sample showed an onset potential of 1.37 V along with required potentials as low as 1.39 and 1.44 V to reach current densities of 10 and 50 mA·cm⁻², respectively. Noteworthy, these values are even lower than those measured for the same sample but for the MOR (e.g. potentials of 1.42 and 1.48 V at 10 and 50 mA·cm⁻², respectively). Moreover, we observed that the ethanol oxidation peak was more pronounced, taking place at a lower voltage, and delivering higher current densities (*i.e.* 108.02 mA·cm⁻² at 1.50 V vs. RHE for the EOR, compared to 81.45 mA·cm⁻² at 1.55 V vs. RHE for MOR), as shown in

Figure 4.8a. These values clearly surpass those observed for the MOR and the OER, unequivocally identifying the $\text{CuCo}_{2/1}$ NCs as a superior catalyst for the EOR. Indeed, we observed that at equal applied voltages, all NCs delivered higher current densities for the EOR compared with the MOR, underlining the effectiveness of these particular nanoheterostructures in catalyzing ethanol oxidation.

Similar to the MOR, we studied the effect of ethanol concentration by increasing the concentration from 0.5 to 4 M (**Figure 4.8d**). We observed a clear activity enhancement as the concentration increased to 1 M. However, further increasing the concentration of ethanol did not result in an increase in activity. Indeed, at a 4 M ethanol concentration, the current density decreased by almost a factor of 1.5 at high voltages (above ca. 1.45 V). This trend suggests the presence of intermediates that remain strongly absorbed by the active sites, reducing ECSA and thereby diminishing efficiency. For instance, an increasing production rate of acetic acid would eventually lead to a local increase of its concentration at the WE interface, displacing the equilibrium and hence decreasing the kinetic of the reaction.

Comparison among OER, MOR and EOR for $\text{CuCo}_{2/1}$

For a straightforward comparison of the OER, MOR, and EOR performance, we focused on $\text{CuCo}_{2/1}$ and compared the applied potentials at 10 and 50 $\text{mA}\cdot\text{cm}^{-2}$. For instance, at 10 $\text{mA}\cdot\text{cm}^{-2}$, the applied potentials for the EOR and the MOR were 157 and 184 mV lower compared to the OER (**Figure 4.9a**). When the current density increased to 50 $\text{mA}\cdot\text{cm}^{-2}$, the gap between the OER and MOR potentials was kept relatively constant (155 mV), whereas that for the EOR further increased to 197 mV. Likewise, the difference between MOR and EOR performances increased from 27 at 10 $\text{mA}\cdot\text{cm}^{-2}$ to 42 mV at 50 $\text{mA}\cdot\text{cm}^{-2}$. The EIS plots for MOR and EOR revealed that the solution resistance (R_s) was comparable (**Figure 4.9b** and **Table 4.1**) for both reactions, with MOR exhibiting similar R_s (5.14 Ω compared to 5.48 Ω for EOR). Additionally, the charge transfer resistance (R_{ct}) for ethanol oxidation (11.73 Ω) was lower than that for methanol oxidation (16.78 Ω), indicating that $\text{CuCo}_{2/1}$ has a lower overall resistance providing faster kinetics for ethanol oxidation, which is in agreement with the observed higher activity for the EOR.

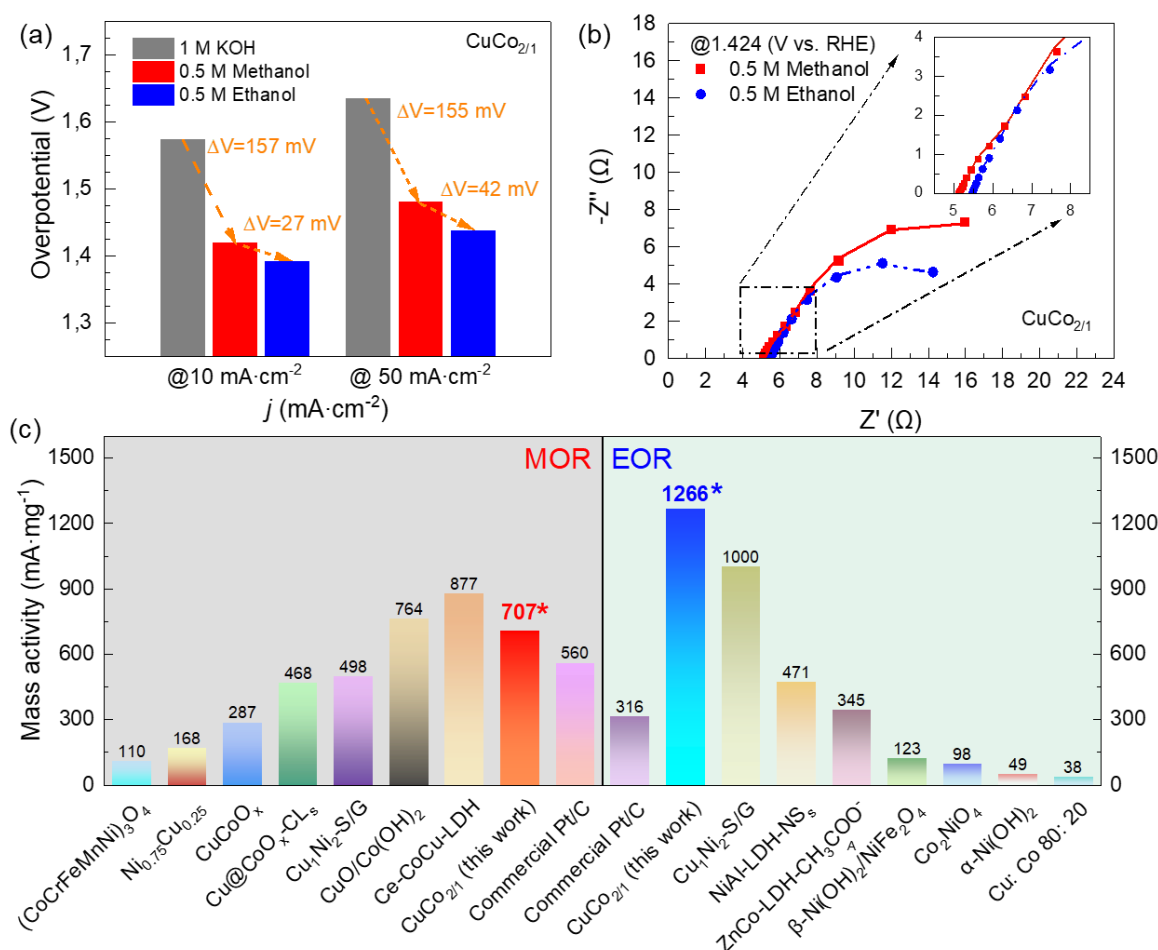


Figure 4.9 (a) Comparison of CuCo_{2/1} for OER, MOR, EOR at applied potentials of 10 and 50 mA·cm⁻². (b) EIS for the CuCo_{2/1} in a KOH electrolyte containing 0.5 M methanol (red squares) or 0.5 M ethanol (blue circles). (c) The comparison of mass activity for CuCo_{2/1} with the state of art for MOR and EOR based on transition metal-based materials and commercial Pt/C (see Table 4.2 and 4.3)

Table 4.1 The values of equivalent circuits of Figure 4.9b

	R_s (Ω)	R_{ct} (Ω)	CPE1-T	CPE1-P
MOR	5.14	16.78	0.0037171	0.9771
EOR	5.48	11.73	0.0026932	0.9336

Finally, the mass activities of the CuCo_{2/1} NCs and commercial Pt/C for the MOR and EOR at 50 mA·cm⁻² were directly compared using the same experimental set-up along with the data reported in the literature for transition metal-based catalysts (Figure 4.9c). For the MOR, CuCo_{2/1} NCs exhibited slightly higher mass activities compared to

commercial Pt/C (707 against $560 \text{ mA}\cdot\text{mg}^{-1}$) and comparable recently reported values on cobalt-copper layer double hydroxide and $\text{CuO}/\text{Co}(\text{OH})_2$ nanosheets ($877 \text{ mA}\cdot\text{mg}^{-1}$ and $764 \text{ mA}\cdot\text{mg}^{-1}$, respectively).^{31,49} Notably, commercial Pt/C exhibits a peak at low applied voltages (0.78 V vs. RHE, [Figure 4.10](#)). However, the relatively low magnitude of this peak significantly limits its overall catalytic activity, as increasing the voltage beyond this point leads to a decline in current density. On the other hand, $\text{CuCo}_{2/1}$ NCs exhibited a rather high mass activity for EOR ($1266 \text{ mA}\cdot\text{mg}^{-1}$), which is significantly higher compared to similar reported works for $\text{Cu}_1\text{Ni}_2\text{-S/G}$ ($1000 \text{ mA}\cdot\text{mg}^{-1}$)⁵⁰ or commercial Pt/C catalyst ($316 \text{ mA}\cdot\text{mg}^{-1}$). Hence, $\text{CuCo}_{2/1}$ NCs showed remarkable mass activities for both alcohol oxidation reactions, similar to or outperforming state-of-the-art Cu-Co-based catalysts. This observation is of particular interest as best performing catalysts for MOR typically do not show high activities for EOR, and vice versa. Overall, $\text{CuCo}_{2/1}$ NCs exhibited dual catalytic activity for both ethanol and methanol oxidation, demonstrating exceptional high performance in the more challenging EOR. These findings prompted a more in-depth characterization of $\text{CuCo}_{2/1}$ NCs to investigate the origin of this enhanced performance.

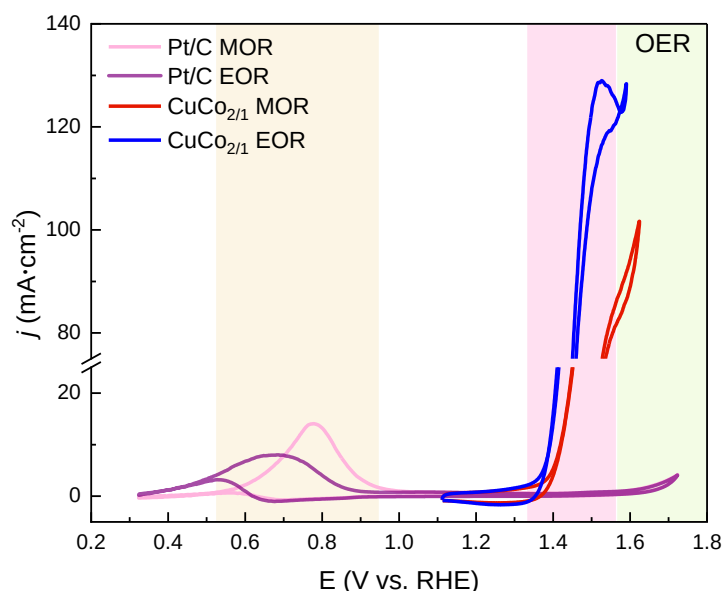


Figure 4.10 The CV measurements for commercial Pt/C and comparison with as-synthesized $\text{CuCo}_{2/1}$ for MOR (1 M KOH + 0.5 M MeOH) and EOR (1 M KOH + 0.5 M EtOH).

Table 4.2 The summary of mass activity of CuCo_{2/1} and the state of the art for MOR

Sample	Mass activity (mA·mg ⁻¹)	Potential (V vs. RHE)	Electrolyte	Supporter	Reference
(CuCrFeMnNi) ₃ O ₄	110	1.624	1 M KOH + 0.5 M MeOH	Ni form	51
Ni _{0.75} Cu _{0.25}	168	1.822	1 M KOH + 0.5 M MeOH	Ti substrate	52
CuCoP _x	287	1.666	1 M KOH + 1 M MeOH	GCE	29
Cu@CoO _x -CLs	468	1.85	1 M KOH + 1 M MeOH	GCE	27
Cu ₁ Ni ₂ -S/G	498	1.50	1 M KOH + 1 M MeOH	Rotating disk electrode (GCE)	50
CuO/Co(OH) ₂	764	1.65	1 M KOH + 3 M MeOH	GCE	49
Ce-CoCu-LDH	877	1.67	1 M KOH + 1 M MeOH	GCE	31
Commercial Pt/C	560	0.78	1 M KOH + 0.5 M MeOH	GCE	This work
CuCo _{2/1}	707	1.50	1 M KOH + 0.5 M MeOH	GCE	

Table 4.3 The summary of mass activity of CuCo_{2/1} and the state of the art for EOR

Sample	Mass activity (mA·mg ⁻¹)	Potential (V vs. RHE)	Electrolyte	Supporter	Reference
Cu:Co 80:20	38	1.60	1 M KOH + 0.1 M EtOH	GCE	33
α-Ni(OH) ₂	49	1.55	1 M KOH + 1 M EtOH	GCE	53
Co ₂ NiO ₄	98	1.60	1 M KOH + 0.1 M EtOH	GCE	54
β-Ni(OH) ₂ /NiFe ₂ O ₄	123	1.524	1 M KOH + 1 M EtOH	GCE	55
ZnCo-LDH-CH ₃ COO ⁻	345	1.666	1 M KOH + 1 M EtOH	GCE	56
NiAl-LDH-NSs	471	1.50	1 M KOH + 1 M EtOH	GCE	57
Cu ₁ Ni ₂ -S/G	1000	1.49	1 M KOH + 1 M EtOH	Rotating disk electrode (GCE)	50
Commercial Pt/C	316	0.68	1 M KOH + 0.5 M EtOH	GCE	This work
CuCo _{2/1}	1266	1.50	1 M KOH + 0.5 M EtOH	GCE	

4.3.3 Characterization of CuCo_{2/1} NCs

The structure of the CuCo_{2/1} NCs was further elucidated through XPS analysis ([Figure 4.11](#)). Deconvolution of the C1s high-resolution spectrum revealed five components with binding energies at 288.7, 287.3, 285.7, 284.8, and 283.6 eV, corresponding to O=C=O, C=O, C-OH, C-C, and metal carbide, respectively ([Figure 4.11b](#)). The carbide signal was later correlated to cobalt carbide by analyzing the cobalt 2p high-resolution energy spectrum. The cobalt spectrum was deconvoluted in up to twelve peaks (excluding an LMM Auger peak at 777.0 eV, [Figure 4.11d](#)), with the peaks at 779.2 and 795.3 eV corresponding to the 2p_{3/2} and 2p_{1/2} orbitals of cobalt carbide, respectively. The presence of four satellite peaks at 784.3, 788.4, 801.1 and 803.2 eV associated with the cobalt carbide and Co²⁺ peaks, confirmed the presence of the carbide phase.⁵⁸ Additional peaks were fitted to metallic cobalt (778.0, 794.1 eV), CoO (780.5, 796.5 eV), and Co(OH)₂ (781.9, 797.8 eV). Similarly, the Cu2p XPS spectrum ([Figure 4.11e](#)) revealed twelve peaks, including those for Cu₂O (931.2 and 950.8 eV), metallic copper (932.6 and 952.3 eV), CuO (934.2 and 953.9 eV), and Cu(OH)₂ (935.4 and 955.8 eV), along with satellite peaks associated with CuO (945.0, 943.3, 961.2, and 963.0 eV). The deconvolution of the O 1s spectra ([Figure 4.11c](#)) corroborated the presence of copper and cobalt oxides and hydroxides (CuO - 528.1 eV; CoO - 529.4 eV; Cu₂O - 530.2 eV; Cu(OH)₂ - 531.3 eV; Co(OH)₂ - 532.0 eV), along with C=O and C-O peaks (532.7 and 533.3 eV, respectively). The confirmation by XPS of a carbide phase was unexpected due to the preliminary XRD data and the synthesis conditions. Nonetheless, it has been reported the direct synthesis of Co₂C and Co₃C nanoparticles by the polyol processes as well as the presence of cobalt carbide in the synthesis of metallic cobalt nanoparticles.⁵⁹

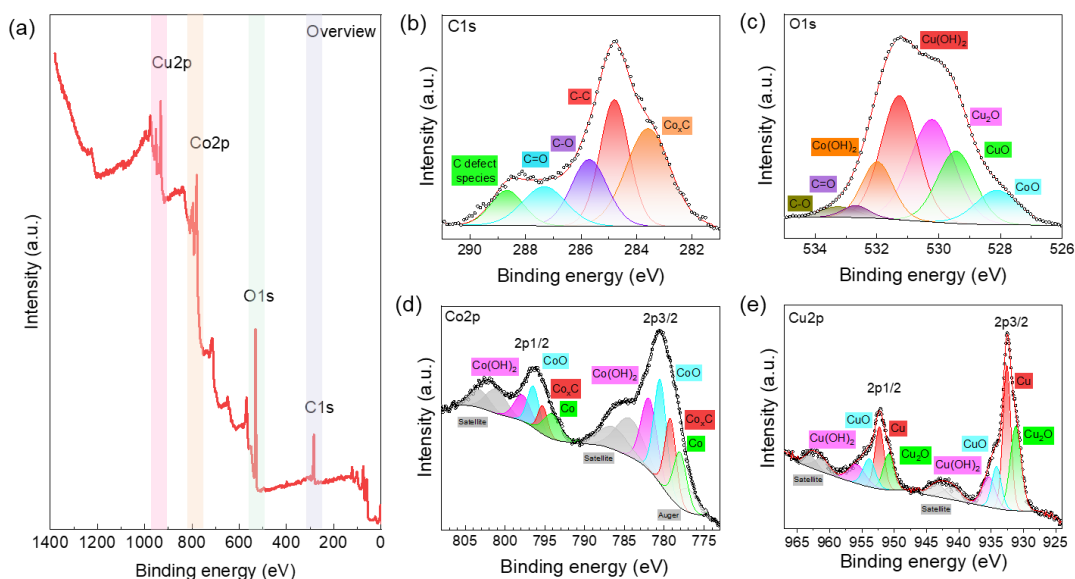


Figure 4.11 (a) XPS overview, (b-e) high resolution XPS spectra in carbon region (C 1s), oxygen region (O 1s), cobalt region (Co 2p) and copper region (Cu 2p).

In order to study the morphology and distribution of the different phases observed by XPS, HR-TEM and EELS analyses were conducted ([Figure 4.12](#)). TEM images clearly reveal a core-shell structure, with a core approximately 50 to 100 nm in diameter surrounded by a 5 to 10 nm thick shell. The measured d-spacing at the core (0.206 nm) matched with the [111] direction of a metallic CuCo structure, while the d-spacing at the shell (0.269 nm) agreed with the [111] direction of a CoO structure ([Figure 4.12c](#)). This confirmed the presence of a metallic core surrounded by a metal oxide shell. As previously mentioned, the core-shell domains are supported on a thin and heterogeneous nanosheet. The analysis of the area corresponding to the nanosheet revealed the presence of crystallographic planes compatible with Cu₂O (0.212 nm, [200]), CoO (0.214 nm, [200]), and Co₂C (0.221 nm, [020]) structures ([Figure 4.12d](#)). This confirms the coexistence of multiple crystallographic phases within the NCs, suggesting the presence of different heterojunctions (e.g., Mott-Schottky) that may serve as catalytic active sites, thereby enhancing the catalytic activity.⁶⁰

The distribution of copper and cobalt was further studied by acquiring EELS and EDX spectrum images of the NCs ([Figure 4.12e-j](#) and [Figure 4.12k-p](#)). The EELS elemental maps shown in [Figure 4.12e-j](#) reveal that Cu-rich areas are surrounded by Co, C, and O regions. EELS analyses performed in different regions of the self-

supported NCs corroborated the concentration of copper at the cores along with traces of cobalt and oxygen in the shell (**Figure 4.13**). Noteworthy, the blunt Cu *L*-edge peak indicates the presence of metallic copper at the core of the NCs,⁶¹ whereas the shell (blue square in **Figure 4.13a**) shows a decrease in the copper signal and a significant increase of the Co, C, and O signals. In particular, the presence of the O signal and the sharpness of the Co *L*-edge indicate the presence of cobalt oxide species.

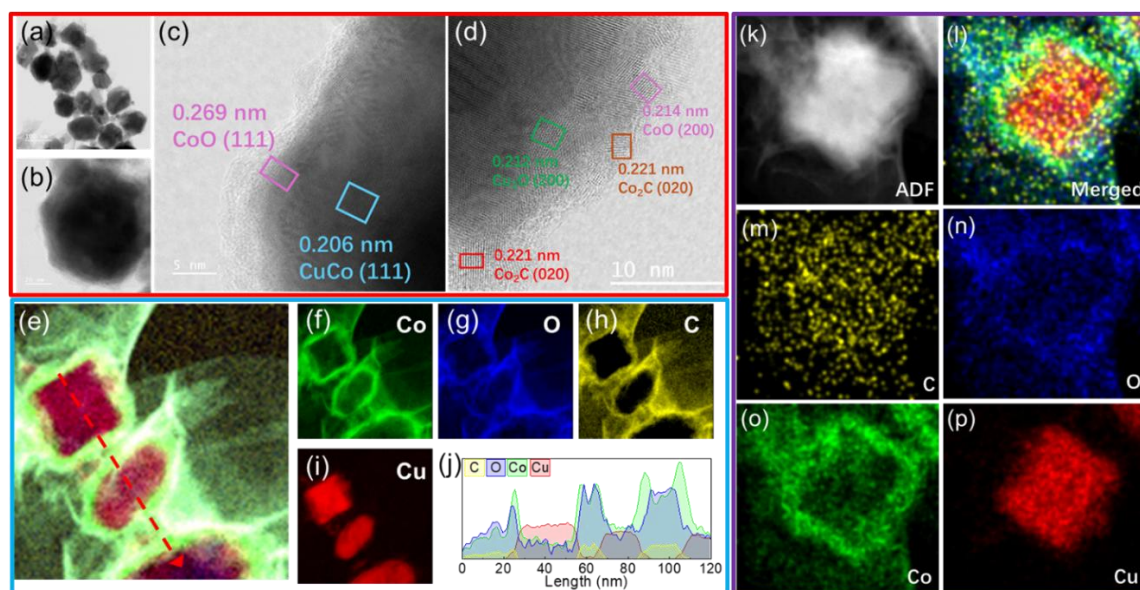


Figure 4.12 (a, b) TEM images at different magnifications, (c), (d) HR-TEM image of $\text{CuCo}_{2/1}$ focusing on nanoparticle or nanosheet, respectively. (e-i) EELS mapping of $\text{CuCo}_{2/1}$, Co, O, C, and Cu, respectively. (j) Profile following the arrow in Fig. 4.12e. EDX mapping of $\text{CuCo}_{2/1}$ NCs (k: ADF, l: merged, m: carbon, n: oxygen, o: cobalt, p: copper)

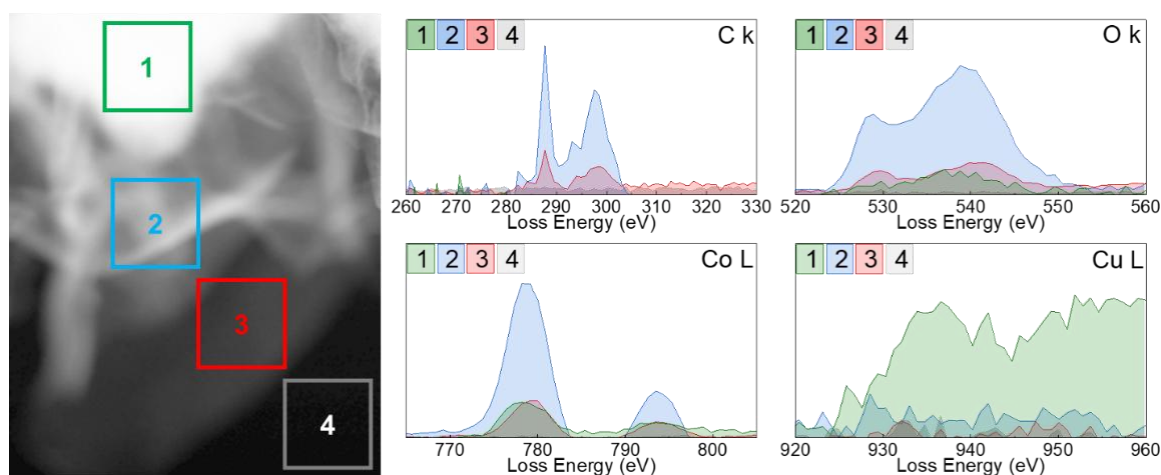


Figure 4.13 EELS C k, O k, Co L, Cu L profiles based on different positions (1 black line: hole, 2 red line: nanosheet, 3 blue line: nanosheet close to nanoparticle, 4 green line: nanoparticle).

In summary, CuCo_{2/1} NCs exhibit a core-shell structure with a Cu-rich metallic core coated by a shell composed of a mixture of copper and cobalt oxides, along with a Co₂C phase. It is important to note that the presence of small amounts of cobalt within the core cannot be entirely ruled out. As for the support, CoO and Co₂C phases extend outward to form the core-shell structure, forming a nanosheet that serves as support. Although CoO and Co₂C were the predominant phases identified through various characterization techniques, a minor presence of copper was detected by EELS mapping. This unique structure comprises the presence of metal-semiconductor and semiconductor-semiconductor heterojunctions, which eventually may lead to an enhancement of the catalytic activity of the core due to the accumulation of charge at the interface.³⁵ Indeed, catalysts comprising heterojunction have been successfully employed for hydrogen production.^{62,63} In our particular case, the additional synergy between the core-shell domain and the nanosheet could ultimately boost the efficiency of the self-supported NCs.

4.3.4 Hybrid Water Electrolysis

To demonstrate the applicability of the CuCo_{2/1} catalyst for hybrid alcohol-water electrolysis, a two-electrode system was set up where the anode and the cathode were functionalized with CuCo_{2/1} NCs and commercial Pt/C, respectively. Both electrodes were prepared by drop-casting the catalyst inks onto carbon cloth (CuCo_{2/1}/CC and Pt/C/CC electrodes). For a comparative evaluation, the CuCo_{2/1}/CC || Pt/C/CC system was tested in three different electrolytes (KOH, KOH + methanol, and KOH + ethanol). First, in 1 M KOH solution (conventional water splitting, [Figure 4.14a](#)), the onset potential was approximately 1.58 V. Current densities of 10, 50, and 100 mA·cm⁻² were achieved under an applied potential of 1.63, 1.75, and 1.83 V, respectively, with a Tafel slope of 161 mV·dec⁻¹. Adding methanol to the electrolyte (1 M KOH and 1 M methanol, hybrid methanol-water splitting) significantly reduced the applied potentials at 10, 50, and 100 mA·cm⁻² ($\Delta V = 221, 203, \text{ and } 171 \text{ mV}$, respectively, [Figure 4.14b](#)). Finally, a similar behavior was observed at lower voltages by adding ethanol (1 M KOH and 1 M ethanol, hybrid ethanol-water electrolysis). In particular, the onset and applied cell potential at low current density (10 mA·cm⁻²) are comparable to hybrid methanol-water electrolysis (1.38 and 1.40 mV, respectively, [Figure 4.14a, b](#)). However, the applied potentials decreased at higher current density compared to methanol ($\Delta V = 18 \text{ and } 7$

mV for 50 and 100 $\text{mA}\cdot\text{cm}^{-2}$, respectively). So did the Tafel slope, showing the lowest value for ethanol among all three electrolytes (141 $\text{mV}\cdot\text{dec}^{-1}$, [Figure 4.14c](#)). This observation aligns with the better EOR performance observed for the $\text{CuCo}_{2/1}$ NCs ([Figure 4.9a](#)), highlighting it as the most promising candidate for hybrid water splitting, simultaneously producing hydrogen along with value-added molecules.

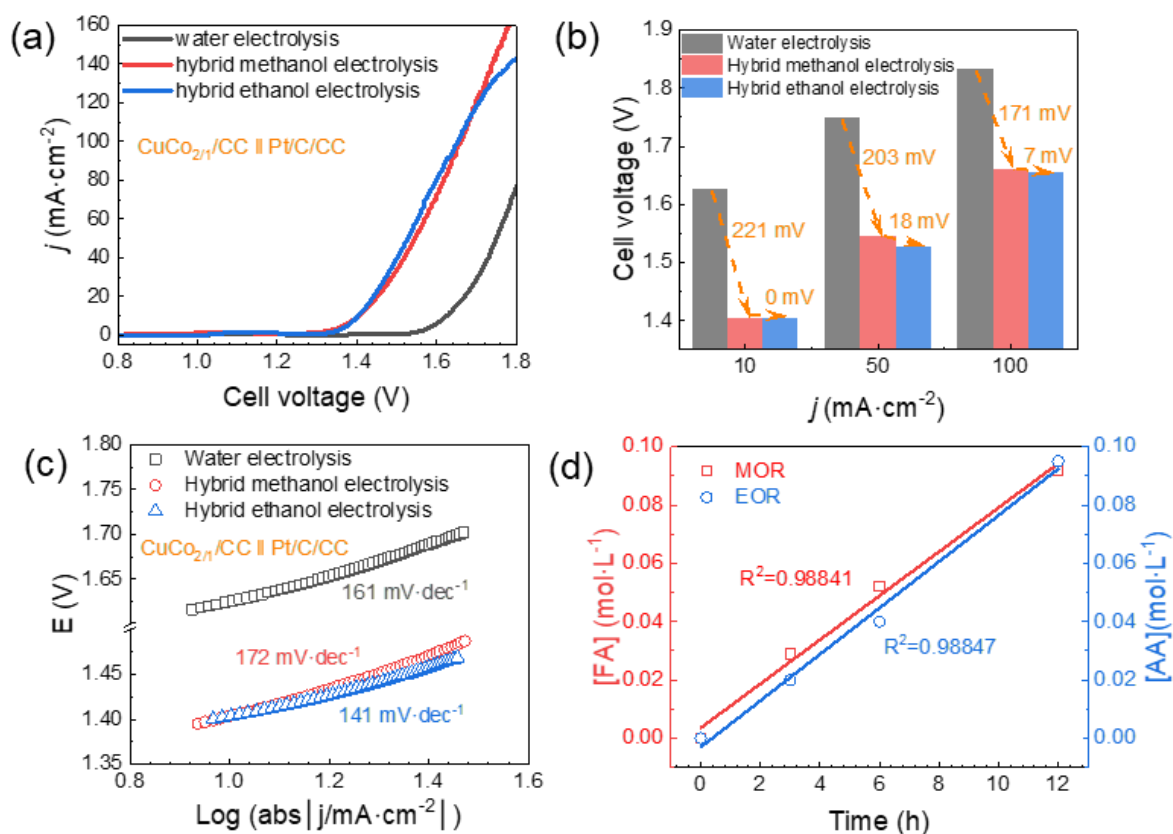


Figure 4.14 (a) LSV polariton curves of hybrid electrolysis (1 M KOH), hybrid methanol electrolysis (1 M KOH + 1 M methanol) and hybrid ethanol electrolysis (1 M KOH + 1 M ethanol) for $\text{CuCo}_{2/1}/\text{CC} \parallel \text{Pt}/\text{C}/\text{CC}$ system. (b) Required cell voltage comparison among water electrolysis, hybrid methanol electrolysis, and hybrid ethanol electrolysis at 10, 50, and 100 $\text{mA}\cdot\text{cm}^{-2}$, respectively. (c) Tafel slopes. (d) Quantification of fitting curves for products during the hybrid methanol or ethanol electrolysis.

Products Characterization

To investigate the reaction products of the aforementioned process, an H-type electrolytic cell was used to separate the alcohol oxidation reaction from the hydrogen evolution reaction while preventing the reduction of products formed from the MOR and the EOR. The products were analyzed via proton and carbon NMR spectroscopy ([Figure 4.14d](#) and [4.15](#)). In the ^{13}C NMR spectrum for the hybrid methanol-water

electrolysis, a peak at 171.59 ppm appeared after 12 hours, indicating the presence of formate in coexistence with methanol (49.50 ppm).⁴⁴ To evaluate the product concentration over time, ^1H NMR spectra were conducted at different time intervals (0, 3, 6, and 12 h), using maleic acid as the internal standard (6.00 ppm, shifting to 6.31 ppm, [Figure 4.15c](#)). The chemical shift observed in [Figure 4.15c](#) is in line with the conversion of maleic acid to fumaric acid via cis-trans isomerization.⁶⁴ Quantitative analysis was performed by integrating the peak areas, resulting in a constant formate production over reaction time ([Figure 4.14d](#)). From these observations, we calculated the Faradaic efficiency for methanol-to-formate conversion, which was found to be 82.2%. This high efficiency underscores the catalyst's effectiveness in selectively producing formate as the primary reaction product.

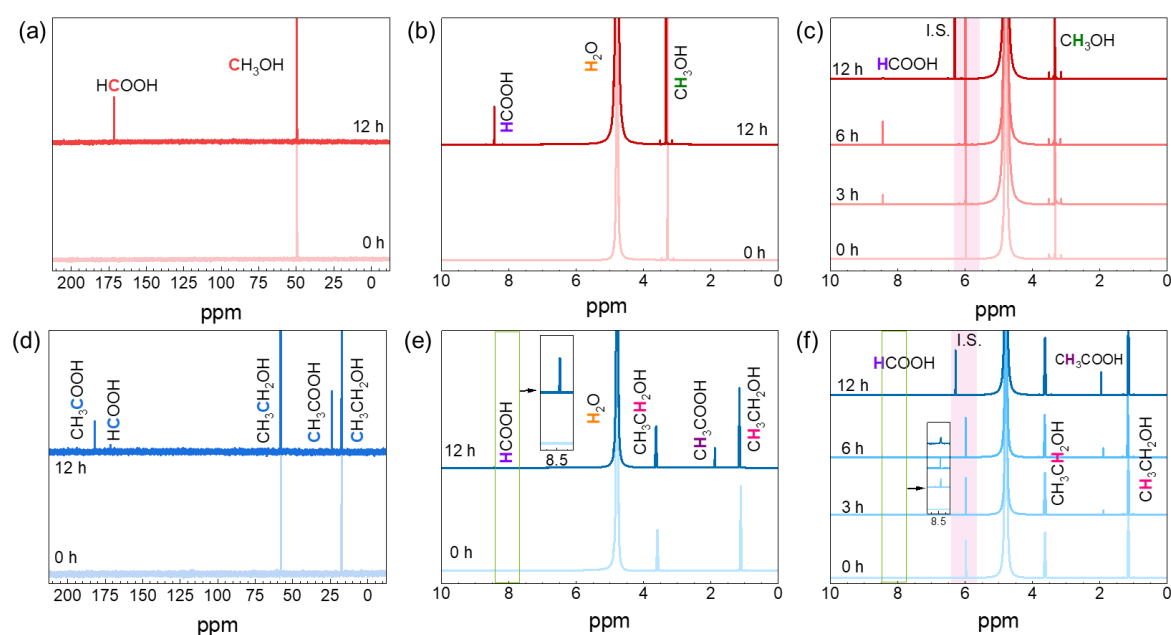


Figure 4.15 (a) ^{13}C NMR analysis of products for hybrid methanol electrolysis for 12 h under $40\text{ mA}\cdot\text{cm}^{-2}$. (b) ^1H NMR analysis of products for hybrid methanol electrolysis for 12 h under $40\text{ mA}\cdot\text{cm}^{-2}$. (c) ^1H NMR analysis of products for hybrid methanol electrolysis for 0, 3, 6, 12 h under $40\text{ mA}\cdot\text{cm}^{-2}$ with internal reference. (d) ^{13}C NMR analysis of products for hybrid ethanol electrolysis for 12 h under $40\text{ mA}\cdot\text{cm}^{-2}$. (e) ^1H NMR analysis of products for hybrid ethanol electrolysis for 12 h under $40\text{ mA}\cdot\text{cm}^{-2}$. (f) ^1H NMR analysis of products for hybrid ethanol electrolysis for 0, 3, 6, 12 h under $40\text{ mA}\cdot\text{cm}^{-2}$ with internal reference.

In the context of hybrid ethanol-water electrolysis, after 12 hours, we observed two peaks corresponding to ethanol at 17.49 and 58.07 ppm, along with two additional

peaks at 23.92 and 182.03 ppm, which can be attributed to the two different carbon environments of acetate ([Figure 4.15d](#)).⁶⁵ Additionally, we observed a small peak at 171.61 ppm, indicating the presence of formate, suggesting that acetate is the primary product of ethanol oxidation, accompanied by a minor amount of formate as a byproduct. This observation is further supported by ¹H NMR results where peaks corresponding to acetate and formate are observed at 1.89 ppm and 8.63 ppm, respectively ([Figure 4.15e, f](#)). The concentration of acetate was determined following the same procedure as in the hybrid methanol-water electrolysis (blue line in [Figure 4.14d](#)). From this data, the selectivity for formate and acetate was 6.1% and 66.7%, respectively, resulting in a total Faradaic efficiency of 91.0% (83.3% for acetate and 7.7% for formate, respectively). Overall, the Faradaic efficiencies for MOR and EOR are comparable to the state-of-the-art, as listed in [Table 4.4](#).

Table 4.4 Comparison of Faradaic efficiencies for MOR and EOR between CuCo_{2/1} NCs and state-of-the-art nanocatalysts.

MOR			EOR		
CuCo _{2/1}	82% @ 1.52 V	this work	CuCo _{2/1}	83.3% @ 1.50 V	this work
CuONS/CF	86.1% @ 1.27 V	66	RuO ₂ -based catalysts	71% @ 1.40 V	67
	97.0% @ 1.36 V			56% @ 1.45 V	
NiCo/(Ni,Co)(O H) _x /C	48.7% @ 0.8 V	68		Ni _{0.75} Co _{0.25} Se ₂	82.9% @ 1.6 V
	~100% @ 1.55 V		76.6% @ 1.5 V		
PtRuNiCoFeGa PbW HEA	~55% @ 0.70 V	20	NiS		51.9% @ 1.4 V
	~47% @ 0.80 V			81% @ 1.60 V	
	~25% @ 0.9 V				
B/CuCo ₂ O ₄	43%*	32	Co-S-P	67.2% @ 1.50 V	71
NiS	98% @ 1.60 V	70	IrO ₂	51%*	72
			IrRuO _x /Ti	67%*	
			Pd ₇₆ Sb ₁₇ Bi ₇ /C	82%*	73
			PtRh NWs/C	43.4% @ 1.0 V	74
			Co ₂ NiO ₄	60% @ 1.55 V	54
			NiOOH-CuO	79.1% @ 1.35 V	65
			Ni(OH) ₂ NSs	92% @ 1.62 V	75
				79% @ 1.52 V	

* Voltage not specified due to lack of explicit information in the cited literature.

Stability Measurements

Finally, we studied the stability of the $\text{CuCo}_{2/1}$ catalyst by performing multistep chronopotentiometry experiments at different current densities (10, 20, 30, 40, and 50 $\text{mA}\cdot\text{cm}^{-2}$). The setup was immersed in a 1 L electrolyte solution containing 1 M KOH and 1 M methanol or ethanol to ensure an adequate alcohol supply. The current was incrementally raised every 6 hours up to 50 $\text{mA}\cdot\text{cm}^{-2}$, where it was kept for 12 hours before decreasing it at the same rate, leading to an overall measurement of 60 hours ([Figure 4.16a](#)). For the hybrid methanol-water electrolysis, the cell voltage increased gradually at each constant current density, with a minimal increase at low current densities (e.g., from 1.40 to 1.43 V at 10 $\text{mA}\cdot\text{cm}^{-2}$ after 6 hours), and a more pronounced increase at higher current densities, reaching 1.73 V at 50 $\text{mA}\cdot\text{cm}^{-2}$ after 12 hours. This difference is clearly observed when considering the slope of the V vs. t curve in [Figure 4.16a](#) for each current density ([Table 4.5](#)). When decreasing the current back to 10 $\text{mA}\cdot\text{cm}^{-2}$, the voltage remained almost constant at high current densities (40 and 30 $\text{mA}\cdot\text{cm}^{-2}$) but slightly increased at low current densities. For instance, from 1.57 to 1.59 V (48 and 53 hours; 30 $\text{mA}\cdot\text{cm}^{-2}$) or from 1.50 to 1.52 V (54 to 60 hours; 10 $\text{mA}\cdot\text{cm}^{-2}$). Indeed, after 60 hours, the final voltage did experience an increase of 0.13 V with respect to the voltage at the same current density but at time zero. The same study was conducted for hybrid ethanol-water electrolysis providing a similar trend. The initial potential of 1.40 V at 10 $\text{mA}\cdot\text{cm}^{-2}$ gradually increased over time, with the applied current density reaching 1.73 V at 50 $\text{mA}\cdot\text{cm}^{-2}$ after 60 hours ([Table 4.5](#)). Nevertheless, when decreasing the applied current density, the cell voltage remained almost constant at any step, delivering a final cell voltage of 1.44 V at 10 $\text{mA}\cdot\text{cm}^{-2}$. This represents an increase with respect to the cell voltage at time zero of 0.04 V (ca. 2.8 %). This underlines the better stability of the NCs for the hybrid ethanol water electrolysis.

The voltage increase over time could be attributed to different factors, such as a rapid consumption of alcohol molecules in solution (methanol or ethanol) during the reaction or the transformation of the NCs. By comparing the LSV curves of the NCs before and after the multistep chronopotentiometry in methanol and ethanol, we observed a significant shift of the curve at higher voltages for the MOR, while for EOR, the curves were maintained ([Figure 4.16b, e](#)). In order to elucidate the influence of alcohol consumption against catalyst transformation, after the chronopotentiometry the

electrolyte was replaced by a fresh solution and additional 6 hours at $10 \text{ mA}\cdot\text{cm}^{-2}$ was carried out ([Figure 4.16c, f](#)). Interestingly, the initial potential for methanol was higher than the initial potential at the start of the multistep chronopotentiometry (1.53 V against 1.40 V) after electrolyte replacement. Conversely, for ethanol, the potential remained consistent (1.41 V). After 6 hours at constant current densities, the cell potential increases (1.56 and 1.44 V for methanol and ethanol, respectively). From this observation, we conclude that hybrid methanol-water electrolysis did have a strong inference in the catalyst structure, while for ethanol, the addition of fresh electrolyte seems to restore the performance completely. This trend was supported by EIS analysis, where the R_{ct} for methanol increased from 0.75Ω up to 3.85Ω after the chronopotentiometry. Remarkably, after replacing the electrolyte, the R_{ct} further increased to 8.49Ω . The same trend was observed for the mass transfer resistance (R_{mt}) of MOR. As for the EOR, the increases in both resistances were moderate but clearly far below those increases observed for MOR. In particular, the R_{mt} values increased within the same order of magnitude (104 to 351Ω). Noteworthy, by replacing the old electrolyte with a fresh one, the resistances for both alcohol oxidation reactions increased. This clearly indicates that the increases measured for the cell voltages during the chronopotentiometry tests are rather related to the evolution of the catalyst's structure.

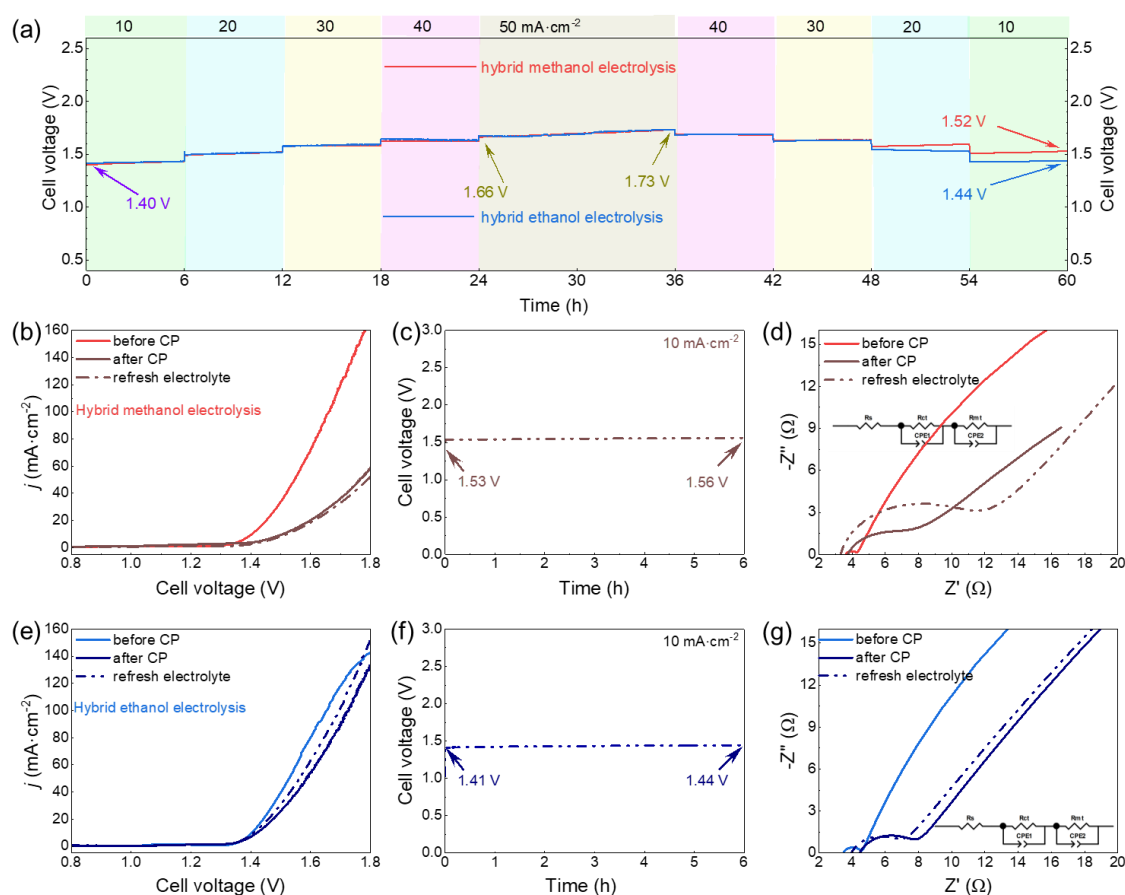


Figure 4.16 (a) Chronopotentiometry of CuCo₂/1/CC || Pt/C/CC system in 1 M KOH + 1 M methanol (red line) and 1 M KOH + 1 M ethanol (blue line). (b) The comparison of CuCo₂/1/CC || Pt/C/CC for hybrid methanol electrolysis before, after 60 h chronopotentiometry, and after refreshing electrolyte. (c) Chronopotentiometry test at 10 mA·cm⁻² for 6 h after refreshing the electrolyte for hybrid methanol electrolysis. (d) The corresponding EIS plots of the time frame in [Figure 4.16b](#). (e) The comparison of CuCo₂/1/CC || Pt/C/CC for hybrid ethanol electrolysis before, after 60 h chronopotentiometry, and after refreshing electrolyte. (f) Chronopotentiometry test at 10 mA·cm⁻² for 6 h after refreshing the electrolyte for hybrid ethanol electrolysis. (g) the corresponding EIS plots of the time frame in [Figure 4.16e](#).

Table 4.5 The summary of potential at different stages of multistep chronopotentiometry in [Figure 4.16a](#)

Current density (mA·cm ⁻²)	Time (h)	Hybrid methanol electrolysis		Hybrid ethanol electrolysis	
		Cell voltage (V)	Difference (V)	Cell voltage (V)	Difference (V)
10	0	1.40		1.41	
	6	1.43		1.43	
20	6	1.48	+0.05	1.49	+0.06
	12	1.52		1.52	
30	12	1.57	+0.05	1.58	+0.06
	18	1.58		1.59	
40	18	1.62	+0.04	1.64	+0.05
	24	1.63		1.63	
50	24	1.66	+0.03	1.68	+0.05
	30	1.70	-	1.69	-
40	36	1.73	-0.04	1.73	-0.03
	36	1.69		1.70	
30	42	1.68	-0.05	1.69	-0.07
	42	1.63		1.62	
20	48	1.63	-0.05	1.63	-0.08
	48	1.58		1.55	
10	54	1.59	-0.08	1.53	-0.10
	54	1.51		1.43	
	60	1.52		1.44	
Overall, above			+0.12		+0.03
Refresh					
10	60+0	1.53		1.41	
	60+10	1.56		1.44	

Table 4.6 The values of equivalent circuits of [Figure 4.16d, g](#)

		R _s (Ω)	R _{ct} (Ω)	CPE1-T	CPE1-P	R _{mt} (Ω)	CPE2-T	CPE2-P
Hybrid methanol electrolysis	before	3.59	0.75	0.0026285	0.63015	74.40	0.050461	0.76747
	after	3.47	3.85	0.00098373	0.76730	5.37E+15	0.046196	0.46900
	refresh	3.31	8.49	0.00063222	0.85688	5.40E+9	0.037530	0.60130
Hybrid ethanol electrolysis	before	3.47	1.12	0.00026536	0.7874	104.10	0.036247	0.78822
	after	4.46	3.30	0.00010484	0.76803	278.30	0.059234	0.64999
	refresh	3.95	2.93	0.0013648	0.77403	351.60	0.061203	0.63194

Post Characterizations for Hybrid Alcohol Electrolysis

A deeper understanding of the structural evolution of the core-shell self-supported nanostructures was obtained by analyzing CuCo_{2/1} NCs after the chronopotentiometry. As shown in [Figure 4.17](#), NCs underwent a significant morphological transformation after the long-term stability test in ethanol, resulting in the formation of self-supported large and elongated nanostructures. These elongated domains show d-lattice spacings corresponding to the [111] plane of CuO, which confirmed the oxidation of the pristine copper core. The shell of the NCs also evolved, resulting in the formation of CoOOH ([021] and [140] planes) and CoO ([220] plane) phases. EDX and EELS elemental mapping of the CuCo_{2/1} NCs confirmed the redistribution of elements along the NCs ([Figure 4.17](#)). Noteworthy, we observed that areas containing both cobalt (778 and 792 eV) and copper (929 and 950 eV) oxides were surrounded by areas in which only one of the oxides was present. The energies and shape of the spectra were in agreement with the oxidation state of cobalt and copper, confirming that the core underwent an oxidation process. This particular configuration would corroborate the outstanding performance of the NCs as CuO domains are surrounded by CoO and CoOOH ones. In particular, the latter have been identified as a true active species for OER, likely acting as active sites boosting the electrocatalytic activity of CuO.⁷⁶ XPS analysis of the NCs after the EOR stability test further supports our findings ([Figure 4.18](#)). A detailed deconvolution of the Co 2p energy region was performed to resolve overlapping components assigned to CoO (780.5 eV, 795.5 eV) and CoOOH (782.3 eV, 797.1 eV). Compared to the spectra of the as-synthesized NCs, the metallic cobalt signals are no longer observed, indicating their transformation. Furthermore, part of the Co²⁺ species is oxidized to CoOOH. Similarly, deconvolution of the Cu 2p region reveals peaks corresponding to metallic Cu (932.7 eV, 952.1 eV), CuO (934.8 eV, 954.3 eV), and CuOOH (936.3 eV, 956.4 eV). While the metallic Cu signal remains detectable, it is significantly diminished, and the emergence of CuOOH indicates partial oxidation of Cu²⁺ to higher-valence states. These findings are consistent with the EELS characterization discussed above, confirming a structural evolution in which Co and Cu atoms diffuse from the metallic core toward the formation of heterojunctions. A similar structure evolution was observed for NCs after chronopotentiometry in the presence of methanol ([Figure 4.19](#)).

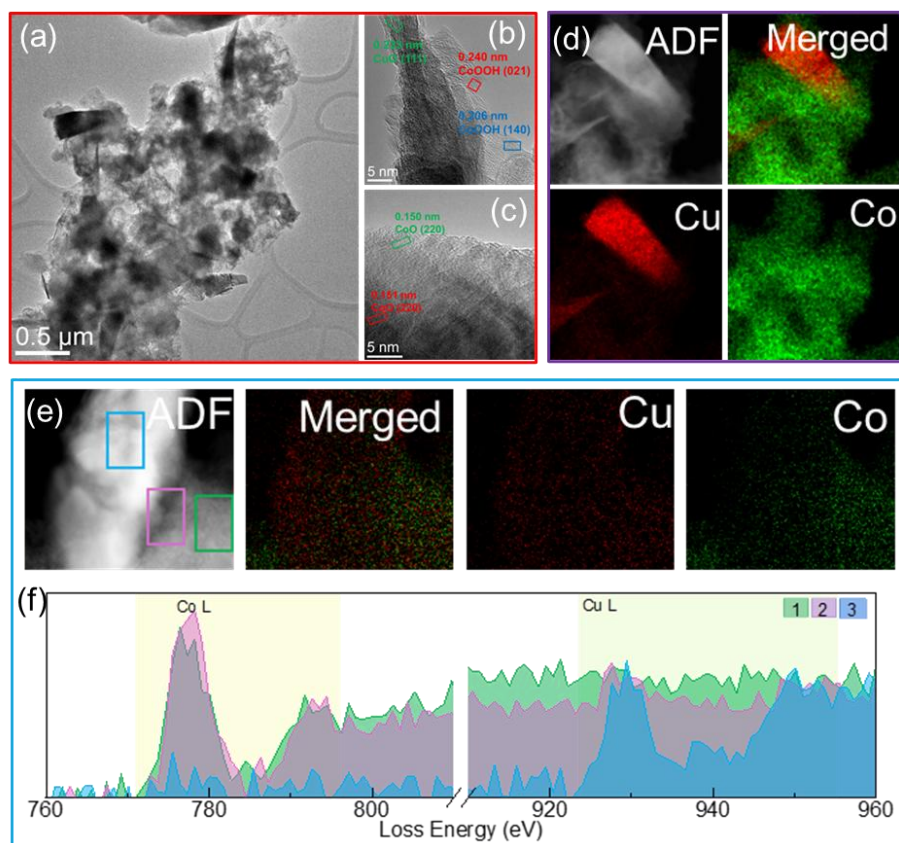


Figure 4.17 (a) TEM image of the $\text{CuCo}_{2/1}$ samples after 60 h chronopotentiometry for hybrid ethanol electrolysis measurement. (b), (c) HR-TEM images focusing on NCs and NPs, respectively. (d), (e) EDX mapping of $\text{CuCo}_{2/1}$ sample after chronopotentiometry test. (f) EELS mapping, (g) profiles of [Figure 4.17e](#) at different positions after hybrid ethanol electrolysis.

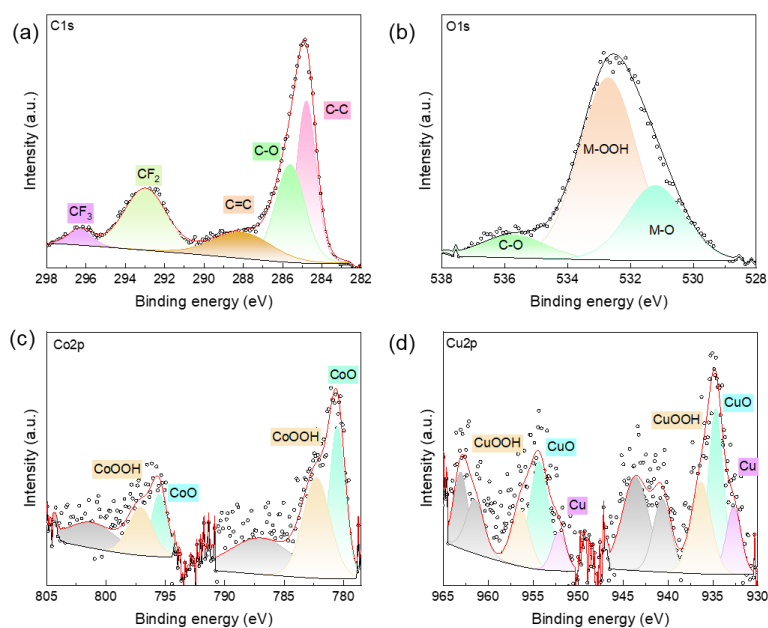


Figure 4.18 High-resolution XPS analysis of the (a) C 1s, (b) O 1s, (c) Co 2p and (d) Cu 2p energy regions for $\text{CuCo}_{2/1}$ NCs after carrying a stability measurement for EOR.

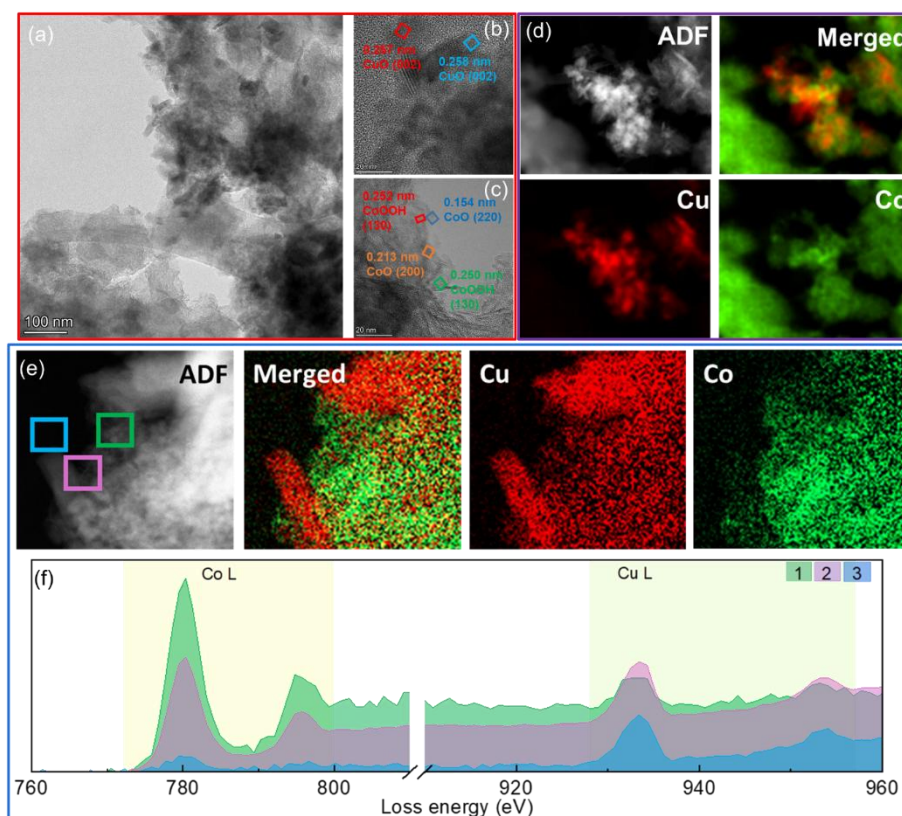


Figure 4.19 (a) TEM image of the $\text{CuCo}_{2/1}$ samples after 60 h chronopotentiometry for hybrid methanol electrolysis measurement. (b), (c) HR-TEM images focusing on NCs and NPs in Figure 4.15 a, respectively. (d), (e) EDX mapping of $\text{CuCo}_{2/1}$ sample after chronopotentiometry. (g) EELS mapping, (h) profiles of Figure 4.19e at different positions after hybrid ethanol electrolysis

4.3.5 Anion Exchange Membrane Hybrid Electrolysis (AEMHE)

As shown in Figure 4.20, the $\text{CuCo}_{2/1}\|\text{Pt}/\text{C}$ electrolysis system results demonstrate that coupling alcohol oxidation as a substitute for the conventional OER can significantly reduce the required applied voltage. As illustrated in Figure 4.20b, achieving j of 100, 200, and 400 $\text{mA}\cdot\text{cm}^{-2}$ in conventional water electrolysis requires applied voltages of 1.937 V, 2.091 V, and 2.269 V, respectively. However, when 1 M methanol is introduced into the electrolyte, the applied voltages decrease to 1.748 V, 1.870V, and 2.002 V. Furthermore, when ethanol oxidation is employed instead of the OER, the required voltages are further reduced to 1.686 V, 1.814 V, and 1.907 V. Compared to conventional water electrolysis, our system achieves a voltage reduction of 362 mV at a current density of 400 $\text{mA}\cdot\text{cm}^{-2}$.

Additionally, compared with the commercial $\text{RuO}_2\|\text{Pt}/\text{C}$ water electrolysis system, while the commercial system exhibits slightly superior performance at lower current

densities ($<200 \text{ mA}\cdot\text{cm}^{-2}$), our system outperforms it at higher current densities. For instance, at $400 \text{ mA}\cdot\text{cm}^{-2}$, our system requires 212 mV less voltage than the commercial system. Moreover, unlike conventional water electrolysis, our system reduces power consumption and generates high-value chemicals at the anode, significantly enhancing economic benefits. Therefore, this strategy offers a promising alternative to traditional electrocatalytic systems by lowering energy consumption and improving overall feasibility.

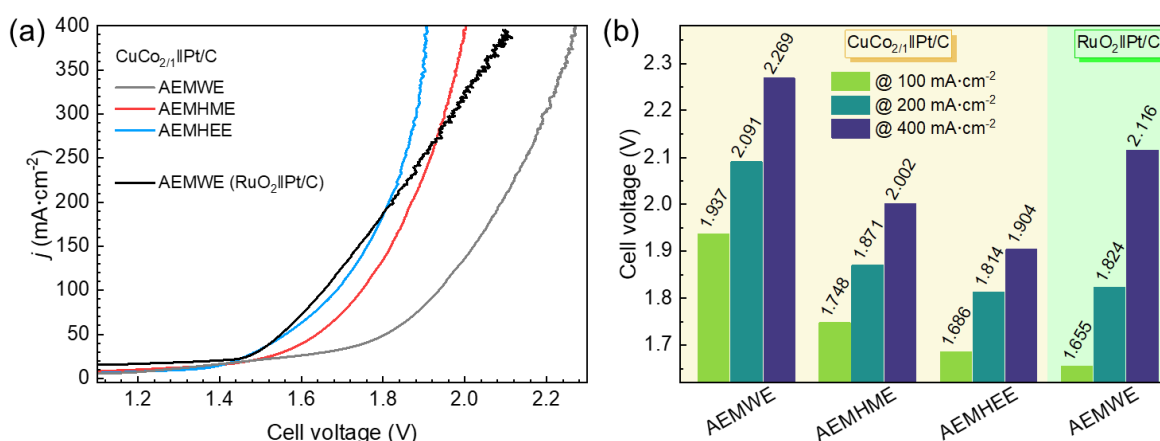


Figure 4.20 The performance comparison of CuCo_{2/1}Pt/C in AEMHE for conventional water splitting, hybrid methanol oxidation, hybrid ethanol oxidation, and benchmark RuO₂Pt/C for OER as a reference.

4.4 Conclusions

We successfully developed a complex yet ordered bimetallic Cu/Co Mott-Schottky nanohybrid structure using a simple and rapid one-pot microwave-assisted method. This structure features a metallic Cu/Co core, surrounded by a mixture of copper oxide, cobalt oxide, and cobalt carbide phases extending into nanosheets providing support for the Cu/Co core. The NCs evolve from the original Mott-Schottky heterostructure into a CuO-CoOOH-CoO composite during electrolysis.

The resulting architecture features a rich array of heterogeneous interfaces, significantly enhancing the oxidation activity toward methanol and ethanol. The observed increase in activity can be attributed to the induced and enhanced self-driven charge transfer within the heterogeneous structure, which balances the adsorption of reactants and the desorption of products. When employing these NCs as anode for alcohol-assisted water electrolysis, potentials are clearly reduced compared to conventional water electrolysis while maintaining stability for over 60 hours. Moreover, alongside the hydrogen evolution reaction, formic and acetic acids are produced at the anode, achieving high selectivity and Faradaic efficiency (91.0% for ethanol oxidation). These findings provide a novel experimental approach for synthesizing multi-interface, high-activity heterogeneous structures, offering additional strategies to address the high cell potential required for conventional water electrolysis and enhancing the overall value of the reaction process.

4.5 References

- 1 Shih, A. J.; Monteiro, M. C. O.; Dattila, F.; Pavesi, D.; Philips, M.; Da Silva, A. H. M.; et al. Water electrolysis. *Nature Reviews Methods Primers* **2022**, 2, 84. <https://doi.org/10.1038/s43586-022-00164-0>.
- 2 Osman, A. I.; Mehta, N.; Elgarahy, A. M.; Hefny, M.; Al-Hinai, A.; Al-Muhtaseb, A. H.; Rooney, D. W. Hydrogen production, storage, utilisation and environmental impacts: a review. *Environmental Chemistry Letters* **2021**, 20 (1), 153-188. <https://doi.org/10.1007/s10311-021-01322-8>.
- 3 Fabbri, E.; Schmidt, T. J. Oxygen evolution reaction-the enigma in water electrolysis. *ACS Catalysis* **2018**, 8 (10), 9765-9774. <https://doi.org/10.1021/acscatal.8b02712>.
- 4 Wang, S.; Lu, A.; Zhong, C.-J. Hydrogen production from water electrolysis: role of catalysts. *Nano Convergence* **2021**, 8, 4. <https://doi.org/10.1186/s40580-021-00254-x>.
- 5 You, B.; Sun, Y. Innovative strategies for electrocatalytic water splitting. *Accounts of Chemical Research* **2018**, 51 (7), 1571-1580. <https://doi.org/10.1021/acs.accounts.8b00002>.
- 6 Yan, D.; Mebrahtu, C.; Wang, S.; Palkovits, R. Innovative electrochemical strategies for hydrogen production: from electricity input to electricity output. *Angewandte Chemie International Edition* **2022**, 62 (16), e202214333. <https://doi.org/10.1002/anie.202214333>.
- 7 Li, D.; Tu, J.; Lu, Y.; Zhang, B. Recent advances in hybrid water electrolysis for energy-saving hydrogen production. *Green Chemical Engineering* **2022**, 4 (1), 17-29. <https://doi.org/10.1016/j.gce.2022.11.001>.
- 8 Wang, T.; Cao, X.; Jiao, L. Progress in hydrogen production coupled with electrochemical oxidation of small molecules. *Angewandte Chemie* **2022**, 134 (51), e202213328. <https://doi.org/10.1002/ange.202213328>.
- 9 Li, D.; Xu, X.; Jiang, J.; Dong, H.; Li, H.; Peng, X.; Chu, P. K. Coupled electrocatalytic hydrogen production. *Materials Science and Engineering R Reports* **2024**, 160, 100829. <https://doi.org/10.1016/j.mser.2024.100829>.
- 10 Eagan, N. M.; Kumbhalkar, M. D.; Buchanan, J. S.; Dumesic, J. A.; Huber, G. W. Chemistries and processes for the conversion of ethanol into middle-distillate fuels. *Nature Reviews Chemistry* **2019**, 3 (4), 223-249. <https://doi.org/10.1038/s41570-019-0084-4>.
- 11 Baruah, B.; Deb, P. Performance and application of carbon-based electrocatalysts in direct methanol fuel cell. *Materials Advances* **2021**, 2 (16), 5344-5364. <https://doi.org/10.1039/d1ma00503k>.
- 12 Wang, J.; Zhang, B.; Guo, W.; Wang, L.; Chen, J.; Pan, H.; Sun, W. Toward electrocatalytic methanol oxidation reaction: longstanding debates and emerging catalysts. *Advanced Materials* **2023**, 35 (26), 2211099. <https://doi.org/10.1002/adma.202211099>.
- 13 Ma, Y.; Wang, X. R.; Li, T.; Zhang, J.; Gao, J.; Sun, Z. Y. Hydrogen and ethanol: production, storage, and transportation. *International Journal of Hydrogen Energy* **2021**, 46 (54), 27330-27348. <https://doi.org/10.1016/j.ijhydene.2021.06.027>.
- 14 Li, J.; Xing, C.; Zhang, Y.; Zhang, T.; Spadaro, M. C.; Wu, Q.; Yi, Y.; He, S.; Llorca, J.; Arbiol, J.; Cabot, A.; Cui, C. Nickel iron diselenide for highly efficient and selective electrocatalytic conversion of methanol to formate. *Small* **2021**, 17 (6), 2006623. <https://doi.org/10.1002/smll.202006623>.
- 15 Hao, Y.; Yu, D.; Zhu, S.; Kuo, C.-H.; Chang, Y.-M.; Wang, L.; Chen, H.-Y.; Shao, M.; Peng, S. Methanol upgrading coupled with hydrogen product at large current density promoted by strong interfacial interactions. *Energy & Environmental Science* **2023**, 16 (3), 1100-1110. <https://doi.org/10.1039/d2ee03936b>.
- 16 Li, R.; Kuang, P.; Wageh, S.; Al-Ghamdi, A. A.; Tang, H.; Yu, J. Potential-dependent reconstruction of Ni-based cuboid arrays for highly efficient hydrogen evolution coupled with

- electro-oxidation of organic compound. *Chemical Engineering Journal* **2022**, 453, 139797. <https://doi.org/10.1016/j.cej.2022.139797>.
- 17 Kodiyath, R.; Ramesh, G. V.; Koudelkova, E.; Tanabe, T.; Ito, M.; Manikandan, M.; Ueda, S.; Fujita, T.; Umezawa, N.; Noguchi, H.; Ariga, K.; Abe, H. Promoted C-C bond cleavage over intermetallic TaPt₃ catalyst toward low-temperature energy extraction from ethanol. *Energy & Environmental Science* **2015**, 8 (6), 1685-1689. <https://doi.org/10.1039/c4ee03746d>.
 - 18 Tan, X.; Chen, S.; Yan, D.; Du, R.; Zhong, Q.; Liao, L.; Tang, Z.; Zeng, F. Recent advances in Ni-based catalysts for the electrochemical oxidation of ethanol. *Journal of Energy Chemistry* **2024**, 98, 588-614. <https://doi.org/10.1016/j.jechem.2024.06.045>.
 - 19 Fu, X.; Wan, C.; Huang, Y.; Duan, X. Noble metal based electrocatalysts for alcohol oxidation reactions in alkaline media. *Advanced Functional Materials* **2022**, 32 (11), 2106401. <https://doi.org/10.1002/adfm.202106401>.
 - 20 Lv, Y.; Liu, P.; Xue, R.; Guo, Q.; Ye, J.; Gao, D.; Jiang, G.; Zhao, S.; Xie, L.; Ren, Y.; Zhang, P.; Wang, Y.; Qin, Y. Cascaded p-d orbital hybridization interaction in ultrathin high-entropy alloy nanowires boosts complete non-CO pathway of methanol oxidation reaction. *Advanced Science* **2024**, 11 (19), 2309813. <https://doi.org/10.1002/advs.202309813>.
 - 21 Zhao, Y.; Björk, E. M.; Yan, Y.; Schaaf, P.; Wang, D. Recent progress in transition metal based catalysts and mechanism analysis for alcohol electrooxidation reactions. *Green Chemistry* **2024**, 26 (9), 4987-5003. <https://doi.org/10.1039/d4gc00227j>.
 - 22 Liu, B.; Xiao, T.; Sun, X.; Peng, H.-Q.; Wang, X.; Zhao, Y.; Zhang, W.; Song, Y.-F. Hierarchical trace copper incorporation activated cobalt layered double hydroxide as a highly selective methanol conversion electrocatalyst to realize energy-matched photovoltaic-electrocatalytic formate and hydrogen co-production. *Journal of Materials Chemistry A* **2022**, 10 (37), 19649-19661. <https://doi.org/10.1039/d2ta01104b>.
 - 23 Wang, J.; Cui, W.; Liu, Q.; Xing, Z.; Asiri, A. M.; Sun, X. Recent progress in cobalt-based heterogeneous catalysts for electrochemical water splitting. *Advanced Materials* **2015**, 28 (2), 215-230. <https://doi.org/10.1002/adma.201502696>.
 - 24 Mao, F.; Qi, Z.; Fan, H.; Sui, D.; Chen, R.; Huang, J. Heterogeneous cobalt catalysts for selective oxygenation of alcohols to aldehydes, esters and nitriles. *RSC Advances* **2017**, 7 (3), 1498-1503. <https://doi.org/10.1039/c6ra27073e>.
 - 25 Duan, X.; Cao, F.; Ding, R.; Li, X.; Li, Q.; Aisha, R.; Zhang, S.; Hua, K.; Rui, Z.; Wu, Y.; Li, J.; Li, A.; Liu, J. Cobalt-doping stabilized active and durable sub-2 nm Pt nanoclusters for low-Pt-loading PEMFC cathode. *Advanced Energy Materials* **2022**, 12 (13), 2103144. <https://doi.org/10.1002/aenm.202103144>.
 - 26 Zhang, B.-W.; Sheng, T.; Wang, Y.-X.; Qu, X.-M.; Zhang, J.-M.; Zhang, Z.-C.; Liao, H.-G.; Zhu, F.-C.; Dou, S.-X.; Jiang, Y.-X.; Sun, S.-G. Platinum-cobalt bimetallic nanoparticles with Pt skin for electro-oxidation of ethanol. *ACS Catalysis* **2016**, 7 (1), 892-895. <https://doi.org/10.1021/acscatal.6b03021>.
 - 27 Sun, Y.; Zhou, Y.; Zhu, C.; Tu, W.; Wang, H.; Huang, H.; Liu, Y.; Shao, M.; Zhong, J.; Lee, S.-T.; Kang, Z. Synergistic Cu@CoO_x core-cage structure on carbon layers as highly active and durable electrocatalysts for methanol oxidation. *Applied Catalysis B: Environment and Energy* **2018**, 244, 795-801. <https://doi.org/10.1016/j.apcatb.2018.12.017>.
 - 28 Madadi, M.; Salarizadeh, P.; Moghadam, M. R.; Bazmandegan-Shamili, A. CuCo₂O₄ supported graphene quantum dots as a new and promising catalyst for methanol oxidation reaction. *Journal of Electroanalytical Chemistry* **2023**, 941, 117532. <https://doi.org/10.1016/j.jelechem.2023.117532>.
 - 29 Zhao, F.; Yang, H.; Qin, K.; Cui, G.; Liu, Q. Three-dimensional heterogeneous copper cobalt phosphides nanoflowers for enhancing catalytic performance for electro-oxidation of methanol. *Journal of the Taiwan Institute of Chemical Engineers* **2021**, 126, 244-251. <https://doi.org/10.1016/j.jtice.2021.06.054>.

- 30 Saxena, A.; Kapila, S.; Medvedeva, J. E.; Nath, M. Copper cobalt selenide as a bifunctional electrocatalyst for the selective reduction of CO₂ to carbon-rich products and alcohol oxidation. *ACS Applied Materials & Interfaces* **2023**, *15* (11), 14433-14446. <https://doi.org/10.1021/acsami.3c00488>.
- 31 Yang, H.; Liu, X.; Qin, K.; Bu, Q.; Liu, Q. Enhancement strategy of photoelectrocatalytic activity of cobalt-copper layer double hydroxide toward methanol oxidation: cerium doping and modification with porphyrin. *Inorganic Chemistry* **2022**, *61* (19), 7414-7425. <https://doi.org/10.1021/acs.inorgchem.2c00438>.
- 32 R, N. K. T.; Kamalakannan, S.; Prakash, M.; Viswanathan, B.; Neppolian, B. Boron-induced cationic vacancy on copper cobalt oxide toward formate selectivity: new insights into methanol oxidation reaction. *ACS Applied Energy Materials* **2022**, *5* (2), 2104-2111. <https://doi.org/10.1021/acsaem.1c03643>.
- 33 Braun, M.; Behrendt, G.; Krebs, M. L.; Dimitri, P.; Kumar, P.; Sanjuán, I.; Cychy, S.; Brix, A. C.; Morales, D. M.; Hörlöck, J.; Hartke, B.; Muhler, M.; Schuhmann, W.; Behrens, M.; Andronescu, C. Electrooxidation of alcohols on mixed copper-cobalt hydroxycarbonates in alkaline solution. *ChemElectroChem* **2022**, *9* (13), e2200267. <https://doi.org/10.1002/celec.202200267>.
- 34 Sheng, S.; Ye, K.; Gao, Y.; Zhu, K.; Yan, J.; Wang, G.; Cao, D. Simultaneously boosting hydrogen production and ethanol upgrading using a highly-efficient hollow needle-like copper cobalt sulfide as a bifunctional electrocatalyst. *Journal of Colloid and Interface Science* **2021**, *602*, 325-333. <https://doi.org/10.1016/j.jcis.2021.06.001>.
- 35 Xu, D.; Zhang, S.-N.; Chen, J.-S.; Li, X.-H. Design of the synergistic rectifying interfaces in Mott-Schottky catalysts. *Chemical Reviews* **2022**, *123* (1), 1-30. <https://doi.org/10.1021/acs.chemrev.2c00426>.
- 36 Lu, X.; Ma, Z.; Chang, Y.; Wang, S.; Li, X.; Xu, D.; Bao, J.; Liu, Y. Mott-Schottky construction boosted plasmon thermal and electronic effects on the Ag/CoV-LDH nanohybrids for highly-efficient water oxidation. *Advanced Materials* **2024**, *36* (29), 2313057. <https://doi.org/10.1002/adma.202313057>.
- 37 He, K.; Tsega, T. T.; Liu, X.; Zai, J.; Li, X.; Liu, X.; Li, W.; Ali, N.; Qian, X. Utilizing the space-charge region of the FeNi-LDH/CoP p-n junction to promote performance in oxygen evolution electrocatalysis. *Angewandte Chemie* **2019**, *131* (34), 12029-12035. <https://doi.org/10.1002/ange.201905281>.
- 38 Yabushita, M.; Neya, A.; Endo, K.; Nakaya, M.; Kanie, K.; Muramatsu, A. Simple liquid-phase synthesis of cobalt carbide (Co₂C) nanoparticles and their use as durable electrocatalysts. *MATERIALS TRANSACTIONS* **2021**, *62* (11), 1632-1638. <https://doi.org/10.2320/matertrans.mt-m2021147>.
- 39 Xuan, C.; Shen, T.; Hou, B. Ni/Fe₂O₃ Mott-Schottky heterointerface engineering and phosphate doping synergistically refining d-band center for efficient oxygen evolution reaction. *Chemical Engineering Journal* **2023**, *479*, 147723. <https://doi.org/10.1016/j.cej.2023.147723>.
- 40 Yuan, M.; Chen, J.; Bai, Y.; Liu, Z.; Zhang, J.; Zhao, T.; Wang, Q.; Li, S.; He, H.; Zhang, G. Unveiling electrochemical urea synthesis by Co-activation of CO₂ and N₂ with Mott-Schottky Heterostructure Catalysts. *Angewandte Chemie International Edition* **2021**, *60* (19), 10910-10918. <https://doi.org/10.1002/anie.202101275>.
- 41 Dong, Q.; Wang, H.; Liu, F.; Ren, J.; Wang, H.; Wang, X.; Wang, R. Cu-Co bimetallic nanocluster Mott-Schottky interaction increasing oxygen reduction reaction activity in rechargeable Zn-air batteries. *Journal of Materials Chemistry A* **2023**, *11* (9), 4717-4728. <https://doi.org/10.1039/d2ta09851b>.
- 42 Torras, M.; Roig, A. Copper oxide nanocubes wrapping metals by microwave synthesis. *Crystal Growth & Design* **2021**, *21* (9), 5027-5035. <https://doi.org/10.1021/acs.cgd.1c00462>.

- 43 McCrory, C. C. L.; Jung, S.; Peters, J. C.; Jaramillo, T. F. Benchmarking heterogeneous electrocatalysts for the oxygen evolution reaction. *Journal of the American Chemical Society* **2013**, *135* (45), 16977-16987. <https://doi.org/10.1021/ja407115p>.
- 44 Shao, J.; Fang, Y.; Wu, X.; Abdullah, M. I.; Tao, Y. Unraveling the role of NiSnPH@OOH/CC perovskite hydroxide for efficient electrocatalytic oxidation of methanol to formate. *Nano Research* **2023**, *17* (4), 2388-2399. <https://doi.org/10.1007/s12274-023-6078-z>.
- 45 Carroll, K. J.; Reveles, J. U.; Shultz, M. D.; Khanna, S. N.; Carpenter, E. E. Preparation of elemental Cu and Ni nanoparticles by the polyol method: an experimental and theoretical approach. *The Journal of Physical Chemistry C* **2011**, *115* (6), 2656-2664. <https://doi.org/10.1021/jp1104196>.
- 46 Zhong, X.; Zhang, Y.; Geng, Z.; Shi, F.; Jiang, M.; Sun, Y.; Wu, X.; Huang, K.; Feng, S. Engineering Cu₂O/Cu@CoO hierarchical nanospheres: synergetic effect of fast charge transfer cores and active shells for enhanced oxygen evolution reaction. *Inorganic Chemistry Frontiers* **2019**, *6* (7), 1660-1666. <https://doi.org/10.1039/c9qi00400a>.
- 47 Chen, Y.; Mao, J.; Zhou, H.; Xing, L.; Qiao, S.; Yuan, J.; Mei, B.; Wei, Z.; Zhao, S.; Tang, Y.; Liu, C. Coordination shell dependent activity of CuCo diatomic catalysts for oxygen reduction, oxygen evolution, and hydrogen evolution reaction. *Advanced Functional Materials* **2023**, *34* (10), 2311664. <https://doi.org/10.1002/adfm.202311664>.
- 48 Zhang, J.; Zhang, C.; Duo, X.; Liu, Z.; Liu, C.; Guo, L.; Xie, A.; Luo, S. Self-assembled acicular CuCo-MOF for enhancing oxygen evolution reaction. *Ionics* **2020**, *26* (10), 5123-5132. <https://doi.org/10.1007/s11581-020-03651-0>.
- 49 Chen, L.; Hua, Z.; Shi, J.; He, M. CuO/Co(OH)₂ nanosheets: a novel kind of electrocatalyst for highly efficient electrochemical oxidation of methanol. *ACS Applied Materials & Interfaces* **2018**, *10* (45), 39002-39008. <https://doi.org/10.1021/acsami.8b16256>.
- 50 Wang, Z.; Liao, X.; Zhou, M.; Huang, F.; Owusu, K. A.; Li, J.; Lin, Z.; Sun, Q.; Hong, X.; Sun, C.; Cheng, Y.; Zhao, Y.; Mai, L. Interfacial and vacancies engineering of copper nickel sulfide for enhanced oxygen reduction and alcohols oxidation activity. *Energy & Environment Materials* **2022**, *6* (5), e12409. <https://doi.org/10.1002/eem2.12409>.
- 51 Talluri, B.; Yoo, K.; Kim, J. High entropy spinel metal oxide (CoCrFeMnNi)₃O₄ nanoparticles as novel efficient electrocatalyst for methanol oxidation and oxygen evolution reactions. *Journal of Environmental Chemical Engineering* **2021**, *10* (1), 106932. <https://doi.org/10.1016/j.jece.2021.106932>.
- 52 Cui, X.; Xiao, P.; Wang, J.; Zhou, M.; Guo, W.; Yang, Y.; He, Y.; Wang, Z.; Yang, Y.; Zhang, Y.; Lin, Z. Highly branched metal alloy networks with superior activities for the methanol oxidation reaction. *Angewandte Chemie International Edition* **2017**, *56* (16), 4488-4493. <https://doi.org/10.1002/anie.201701149>.
- 53 Liang, W.; Wang, Y.; Zhao, L.; Guo, W.; Li, D.; Qin, W.; Wu, H.; Sun, Y.; Jiang, L. 3D anisotropic Au@Pt-Pd hemispherical nanostructures as efficient electrocatalysts for methanol, ethanol, and formic acid oxidation reaction. *Advanced Materials* **2021**, *33* (30), 2100713. <https://doi.org/10.1002/adma.202100713>.
- 54 Michaud, S. E.; Barber, M. M.; Cruz, K. E. R.; McCrory, C. C. L. Electrochemical oxidation of primary alcohols using a Co₂NiO₄ catalyst: effects of alcohol identity and electrochemical bias on product distribution. *ACS Catalysis* **2022**, *13* (1), 515-529. <https://doi.org/10.1021/acscatal.2c02923>.
- 55 Chen, L.; Yang, X.; Gao, Y.; Tian, Y.; Wang, Y.; Zhao, X.; Lei, X.; Zhang, F. β-Ni(OH)₂/NiFe₂O₄ heterostructure composite derived from layered double hydroxides precursor for ethanol oxidation electrocatalysis. *International Journal of Hydrogen Energy* **2023**, *48* (67), 26148-26161. <https://doi.org/10.1016/j.ijhydene.2023.03.242>.

- 56 Yang, H.; Guo, T.; Qin, K.; Liu, Q. Different interlayer anions controlled zinc cobalt layered double hydroxide nanosheets for ethanol electrocatalytic oxidation. *The Journal of Physical Chemistry C* **2021**, 125 (45), 24867-24875. <https://doi.org/10.1021/acs.jpcc.1c06449>.
- 57 Xu, L.; Wang, Z.; Chen, X.; Qu, Z.; Li, F.; Yang, W. Ultrathin layered double hydroxide nanosheets with Ni(III) active species obtained by exfoliation for highly efficient ethanol electrooxidation. *Electrochimica Acta* **2017**, 260, 898-904. <https://doi.org/10.1016/j.electacta.2017.12.065>.
- 58 Wu, Y.; Xiao, Z.; Jin, Z.; Li, X.; Chen, Y. The cobalt carbide/bimetallic CoFe phosphide dispersed on carbon nanospheres as advanced bifunctional electrocatalysts for the ORR, OER, and rechargeable Zn-air batteries. *Journal of Colloid and Interface Science* **2021**, 590, 321-329. <https://doi.org/10.1016/j.jcis.2021.01.055>.
- 59 Yang, W.; Rehman, S.; Chu, X.; Hou, Y.; Gao, S. Transition metal (Fe, Co and Ni) carbide and nitride nanomaterials: structure, chemical synthesis and applications. *ChemNanoMat* **2015**, 1 (6), 376-398. <https://doi.org/10.1002/cnma.201500073>.
- 60 Pal, S.; Ahmed, T.; Khatun, S.; Roy, P. Heterojunction engineering for electrocatalytic applications. *ACS Applied Energy Materials* **2023**, 6 (15), 7737-7784. <https://doi.org/10.1021/acsaem.3c01058>.
- 61 Pearson, D. H.; Ahn, C. C.; Fultz, B. White lines and d-electron occupancies for the 3d and 4d transition metals. *Physical Review. B, Condensed Matter* **1993**, 47 (14), 8471-8478. <https://doi.org/10.1103/physrevb.47.8471>.
- 62 Hou, J.; Sun, Y.; Wu, Y.; Cao, S.; Sun, L. Promoting active sites in core-shell nanowire array as Mott-Schottky electrocatalysts for efficient and stable overall water splitting. *Advanced Functional Materials* **2017**, 28 (4), 1704447. <https://doi.org/10.1002/adfm.201704447>.
- 63 Wu, M.; Zhao, J.; Li, C.; Liu, R. Heterogeneity in a metal-organic framework in situ guides engineering Co@CoO heterojunction for electrocatalytic H₂ production in tandem with glucose oxidation. *Journal of Materials Chemistry A* **2022**, 10 (9), 4791-4799. <https://doi.org/10.1039/d1ta10903k>.
- 64 Chen, W.; Chen, X.; Yi, S. Kinetic study on the preparation of fumaric acid from maleic acid by batch noncatalytic isomerization. *ACS Omega* **2019**, 4 (5), 8274-8281. <https://doi.org/10.1021/acsomega.9b00316>.
- 65 Sun, H.; Li, L.; Chen, Y.; Kim, H.; Xu, X.; Guan, D.; Hu, Z.; Zhang, L.; Shao, Z.; Jung, W. Boosting ethanol oxidation by NiOOH-CuO nano-heterostructure for energy-saving hydrogen production and biomass upgrading. *Applied Catalysis B: Environment and Energy* **2023**, 325, 122388. <https://doi.org/10.1016/j.apcatb.2023.122388>.
- 66 Wei, X.; Li, Y.; Chen, L.; Shi, J. Formic acid electro-synthesis by concurrent cathodic CO₂ reduction and anodic CH₃OH oxidation. *Angewandte Chemie International Edition* **2020**, 60 (6), 3148-3155. <https://doi.org/10.1002/anie.202012066>.
- 67 Kohlhaas, I.; Kurig, N.; Palkovits, R. Electrochemical ethanol oxidation using RuO₂-based catalysts: suppressing OER and tailored switching between water oxidation and ethanol oxidation. *ChemElectroChem* **2024**, 11 (10), e202300753. <https://doi.org/10.1002/celec.202300753>.
- 68 Pei, A.; Xie, R.; Zhu, L.; Wu, F.; Huang, Z.; Pang, Y.; Chang, Y.-C.; Chai, G.; Pao, C.-W.; Gao, Q.; Shang, C.; Li, G.; Ye, J.; Zhu, H.; Yang, Z.; Guo, Z. Methanol-enhanced low-cell-voltage hydrogen generation at industrial-grade current density by triadic active sites of Pt₁-Pd_n-(Ni,Co)(OH)_x. *Journal of the American Chemical Society* **2025**, 147 (4), 3185-3194. <https://doi.org/10.1021/jacs.4c12665>.
- 69 Li, J.; Wang, X.; Xing, C.; Li, L.; Mu, S.; Han, X.; He, R.; Liang, Z.; Martinez, P.; Yi, Y.; Wu, Q.; Pan, H.; Arbiol, J.; Cui, C.; Zhang, Y.; Cabot, A. Electrochemical reforming of ethanol with acetate Co-production on nickel cobalt selenide nanoparticles. *Chemical Engineering Journal* **2022**, 440, 135817. <https://doi.org/10.1016/j.cej.2022.135817>.

- 70 Li, J.; Tian, X.; Wang, X.; Zhang, T.; Spadaro, M. C.; Arbiol, J.; Li, L.; Zuo, Y.; Cabot, A. Electrochemical conversion of alcohols into acidic commodities on nickel sulfide nanoparticles. *Inorganic Chemistry* **2022**, *61* (34), 13433-13441. <https://doi.org/10.1021/acs.inorgchem.2c01695>.
- 71 Sheng, S.; Ye, K.; Sha, L.; Zhu, K.; Gao, Y.; Yan, J.; Wang, G.; Cao, D. Rational design of Co-S-P nanosheet arrays as bifunctional electrocatalysts for both ethanol oxidation reaction and hydrogen evolution reaction. *Inorganic Chemistry Frontiers* **2020**, *7* (22), 4498-4506. <https://doi.org/10.1039/d0qi00289e>.
- 72 Tian, C.; Li, X.-Y.; Nelson, V. E.; Ou, P.; Zhou, D.; Chen, Y.; et al. Paired electrosynthesis of H₂ and acetic acid at A/cm² current densities. *ACS Energy Letters* **2023**, *8* (10), 4096-4103. <https://doi.org/10.1021/acsenergylett.3c01327>.
- 73 Wang, Q.; Li, T.; Yan, S.; Zhang, W.; Lv, G.; Xu, H.; Li, H.; Wang, Y.; Liu, J. Boosting hydrogen production by selective anodic electrooxidation of ethanol over trimetallic PdSbBi nanoparticles: composition matters. *Inorganic Chemistry* **2022**, *61* (40), 16211-16219. <https://doi.org/10.1021/acs.inorgchem.2c02888>.
- 74 Zhu, Y.; Bu, L.; Shao, Q.; Huang, X. Subnanometer PtRh nanowire with alleviated poisoning effect and enhanced C-C bond cleavage for ethanol oxidation electrocatalysis. *ACS Catalysis* **2019**, *9* (8), 6607-6612. <https://doi.org/10.1021/acscatal.9b01375>.
- 75 Zhang, Z.; Dong, Y.; Carlos, C.; Wang, X. Surface ligand modification on ultrathin Ni(OH)₂ nanosheets enabling enhanced alkaline ethanol oxidation kinetics. *ACS Nano* **2023**, *17* (17), 17180-17189. <https://doi.org/10.1021/acsnano.3c05014>.
- 76 Ren, X.; Dai, Y.; Wen, X.; Guo, B.; Shi, C.; Huang, X.; Guo, Y.; Li, S. CoOOH: synthesis and application in alkaline electrochemical oxygen evolution reaction. *Advanced Sustainable Systems* **2023**, *8* (3), 2300379. <https://doi.org/10.1002/adsu.202300379>.

Conclusions and Outlook

5.1 General Conclusions

In this thesis, the key electrochemical reactions involved in the production of hydrogen, including direct water electrolysis and hybrid alcohol-water electrolysis, were investigated. As mentioned in **Section 1.7.1, Chapter 1**, the overall main objective is the design and synthesis of highly efficient electrocatalysts for the improvement of the overall water-splitting kinetics at optimized energy inputs. During the development of this research, challenges such as the optimization of the active material (e.g., in particular for precious elements such as Pt or Au), structural and compositional evolution, catalytic selectivity towards different reaction (e.g., chlorine evolution reaction, EOR or MOR) and the stability of the catalyst were addressed by developing novel synthetic strategies to design advanced electrocatalysts. In particular, size, morphology, and composition engineering allowed efficient exploitation of the active sites in noble-metal-based electrocatalysts. Similarly, composition control in alloyed NCs delivers core-shell structures that further evolve to advanced self-supported electrocatalysts with selectivity for hybrid water splitting. Finally, the precise control of co-dopants in LDH also resulted in the development of an outstanding electrocatalyst for the OER with outstanding stability under harsh conditions (*i.e.*, direct seawater electrolysis). Overall, these strategies have led to the development of novel advanced electrocatalysts with enhanced activity and stability, expected to have a strong impact on the development of sustainable processes for the mass production of green hydrogen.

Throughout this research project, advanced experimental characterization techniques, such as HR-TEM, NMR, electrochemical activity testing, and DFT simulation, were employed in combination. This integrated approach enabled a comprehensive understanding of catalytic behavior as a function of structure, size, and composition, while also shedding light on the underlying reaction mechanisms of the reported processes. However, it was not possible to conduct in-situ experiments using a high-

energy radiation beam (synchrotron), where more detailed studies and validation of some of the proposed mechanisms could have been achieved. Despite this limitation, a proposal submitted for access to the SOLEIL synchrotron in France (XAS in Beamline Samba, and XPS in Beamline Tempo) has been approved through NFFA-Europe project during the writing of this thesis, opening the door for future in-depth investigations.

Collectively, this work contributes to the rational design of nanostructured catalysts and offers promising directions for the development of cost-effective and efficient systems for sustainable hydrogen production.

5.2 Specific Conclusions and Future Perspectives

In this section, the specific conclusions withdrawn for the previously discussed results (**Chapters 2, 3 and 4**) are summarized.

5.2.1 Synthesis and Performance of Au@Pt Core-shell NCs for HER

MW-assisted Colloidal Synthesis for Metal-alloyed Nanostructures: A rapid and scalable MW-assisted synthesis colloidal synthesis strategy was developed to fabricate a series of AuPt core-shell NCs. Systematic parameter studies revealed that the Au/Pt molar ratio, PVP_{10k} concentration, total metal ion concentration, and HCl concentration strongly influenced nucleation behavior and final NC morphology.

Modulation of the Electrocatalytic Activity on Advanced Heterostructures: The strategic addition of chlorine ions modulated the reaction kinetics of Au and Pt precursors, enabling preferential nucleation of Au, which served as a “seed” for the epitaxial growth of a Pt-rich shell. This architecture enhanced the surface exposure of Pt atoms while minimizing Pt consumption, thereby improving mass activity and cost-efficiency, while Au served as the electron transfer accelerator.

Outperforming Noble-metal Electrocatalysts for the HER: The optimized sample, AuPt_{1/4}Cl, exhibited excellent acidic HER activity. In particular, overpotentials as low as 24 and 51 mV at 10 and 100 mA·cm⁻², respectively, were achieved. The Tafel slope of 13 mV·dec⁻¹ also indicates fast HER kinetics. Finally, a mass activity as high as 13.8 A·mg⁻¹Pt, was achieved. Noteworthy, this activity is 6.9-fold higher than commercial Pt/C. Superior long-term stability for continuous 4000-cycle CVs and 200-hour chronopotentiometry running was achieved. This is in line with the proposed objectives discussed in **Chapter 1 (Obj. 1, Section 1.7.1)**.

Halide Atoms for the Control of Metal-alloyed Nanostructures in MW-assisted Synthesis: In this chapter, we highlight the great potential of chlorine ions to modulate the synthesis kinetics and the final structure of a metal-alloyed nanostructure. Moreover, this research was further extended to other halide atoms as part of Mr. Josep Amorós's bachelor's thesis in 2023, in which bromide and iodide ions were employed to replace chloride ions, revealing that bromide ions can significantly tune the kinetics, while iodide ions produce large aggregates.

Improving the Efficiency in Neutral/Alkaline Media: Despite the outstanding performance of AuPt_{1/4}Cl compared to state-of-the-art electrocatalysts in acidic media, samples of AuPt_{1/4} and AuPt_{1/4}Cl exhibited lower activities compared to commercial Pt/C in neutral and alkaline media for the HER. This limitation is further reflected in the lower performance observed when AuPt catalysts are coupled with B,Al-NiFe LDH (**Chapter 3**) and CuCo_{2/1} (**Chapter 4**), as displayed in [Figure 5.1](#). In particular, the combination of AuPt_{1/4}Cl with those catalysts not only failed to achieve synergistic enhancement but, in some cases, showed inferior activity compared to commercial Pt/C catalysts.

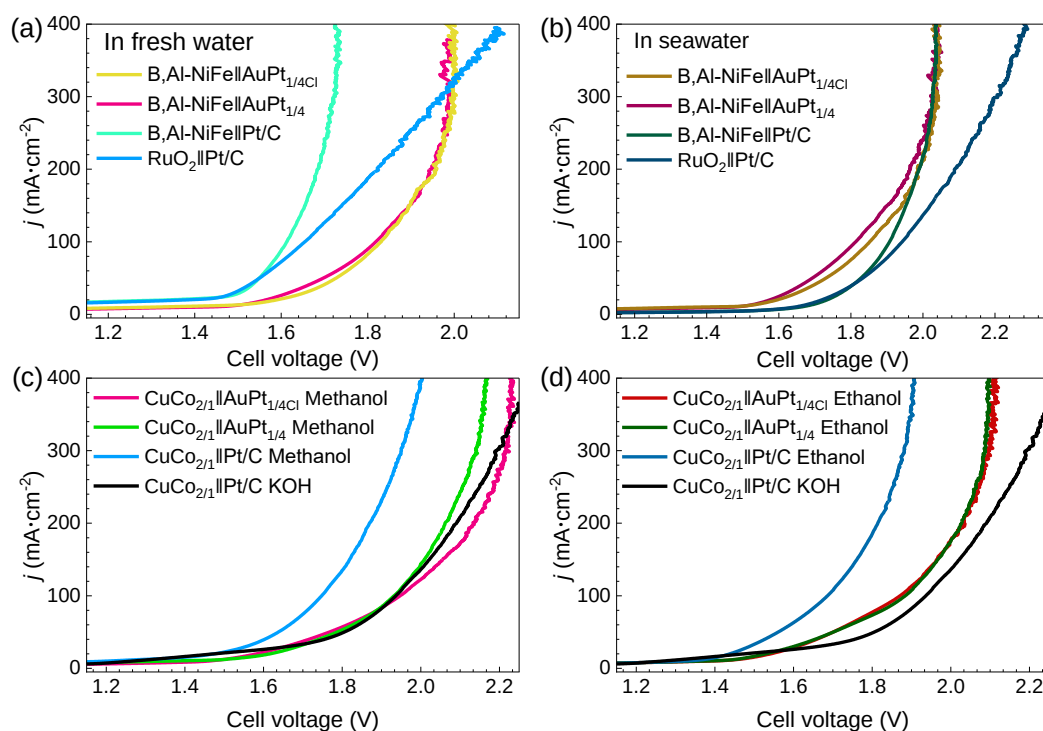


Figure 5.1 Polarization curves of different MEA measured in various electrolyte environments. (a) B,Al-NiFe LDH||AuPt_{1/4}Cl (AuPt_{1/4}, and Pt/C) in fresh water, (b) B,Al-NiFe LDH||AuPt_{1/4}Cl (AuPt_{1/4}, and Pt/C) in seawater, (c) CuCo_{2/1}||AuPt_{1/4}Cl (AuPt_{1/4}, and Pt/C) in methanol solution, and (d) CuCo_{2/1}||AuPt_{1/4}Cl (AuPt_{1/4}, and Pt/C) in ethanol solution. The performance is compared with commercial RuO₂||Pt/C counterparts, highlighting the influence of catalyst composition and electrolyte type on overall cell voltage and current density.

Based on the above discussion, enhancing alkaline HER activity by modulating OH⁻ adsorption/desorption is critical, several strategies can be considered. First, incorporating additional metals such as Ni, Co, or Fe to form alloys or interface-rich heterojunctions can effectively tailor the electronic structure and improve catalytic performance. Second, introducing a hydrophilic surface layer, such as Ni(OH)₂ or Co(OH)₂, can enhance OH⁻ adsorption and facilitate interfacial reactions. Third, employing support materials with strong OH⁻ affinity, including NiFe LDH, alkaline MOFs, or nitrogen-doped carbon, can synergistically strengthen the electrolyte-catalyst interface and reduce interfacial resistance.

Cost Reduction of Noble Metal Catalysts: Given the high cost of AuPt-based nanostructures, future research should focus on partially replacing Au with lower-cost

metals such as Cu, Ag, or Ni while maintaining high catalytic activity. Furthermore, improving catalyst stability under industrial current densities will require advanced surface modification or protective coatings to improve corrosion resistance.

5.2.2 Development of B,Al-NiFe LDH Catalyst for OER

Dual-heteroatom Doping Strategy for Active LDH Design: A dual-doping approach was employed to construct a highly active LDH-based catalyst. The Al-NiFe LDH precursor was first synthesized, followed by post-synthetic B incorporation via wet impregnation. This strategy effectively introduced dual dopants into the LDH lattice, enhancing its catalytic functionality. This contributes to the main goal of this thesis; The rational design of advanced electrocatalyst for hydrogen production.

Defect Engineering and Electronic Structure Modulation: The resulting B,Al-NiFe LDH nanosheets featured a highly defective structure enriched with O_v , which facilitates the LOM pathway for OER. Both experimental characterization and DFT simulation confirmed that B and Al dopants modulated the local electronic environment of Ni and Fe centers, promoting favorable O-O coupling kinetics for oxygen evolution.

Outstanding OER Performance under Alkaline Conditions: The optimized catalyst delivered excellent OER activity, with low overpotentials of 169, 196, and 254 mV at current densities of 10, 100, and 500 $\text{mA}\cdot\text{cm}^{-2}$, respectively. A Tafel slope of $38 \text{ mV}\cdot\text{dec}^{-1}$ highlighted fast reaction kinetics, while an electrochemically active surface area (ECSA) of 254.4 cm^2 reflected the abundance of accessible active sites. The performance achieved completely fulfil **Obj. 2** described in the introduction section.

Robust Durability in Natural Seawater: The catalyst exhibited excellent long-term stability, sustaining continuous operation in natural seawater electrolysis for over 360 hours without significant performance degradation. This stability emphasizes its applicability in practical saline water splitting.

Superior Full-cell Performance Compared to Noble-metal Benchmark: In a two-electrode full-cell configuration (B,Al-NiFe||Pt/C), a significant voltage reduction of 400 mV was achieved compared to the conventional RuO₂||Pt/C benchmark. This highlights the promise of the B,Al-NiFe LDH catalyst as a cost-effective alternative for scalable alkaline and seawater electrolysis systems.

Performance Attenuation in Seawater: Although the catalyst exhibits excellent OER performance in alkaline freshwater, a notable decline in activity is observed in natural seawater, although it outperforms the benchmark. This is likely due to the complex ionic composition and corrosive species present in seawater, which can interfere with active site stability and surface reaction pathways.

Scalability Limitations of Hydrothermal Synthesis: The current hydrothermal approach is constrained by the capacity of autoclave reactors, hindering large-scale production. This limitation presents a major barrier to practical deployment, especially for industrial-scale water electrolysis systems.

Structural Instability and Aluminum Leaching: Direct growth on NF substrates may lead to catalyst delamination under high current and prolonged electrolysis. Furthermore, aluminum, as an amphoteric element, is prone to dissolution under high-pH, high-temperature, or long-term operating conditions, potentially degrading the catalyst structure and reducing durability.

Entropy Engineering for Improved Robustness: Ongoing work collaborating with Ms. Shenqin Guan is exploring medium- or high-entropy LDH systems by incorporating multiple metal species to improve structural stability while keeping or enhancing the activity, suppressing elemental loss, and providing enhanced resistance to corrosive environments such as seawater. Such designs may also enable synergistic catalytic effects and broaden application windows.

5.2.3 Cu@CoO Core-shell NCs for AOR as an OER Alternative

Alcohol Oxidation as an Energy-efficient Anodic Strategy: To improve the overall energy efficiency and economic viability of water electrolysis, the OER was replaced by the oxidation of small organic molecules such as methanol and ethanol. This alternative anodic route significantly reduces the required cell voltage and generates value-added products.

Core-shell Nanostructure via MW-assisted Synthesis: A Cu@CoO core-shell catalyst was synthesized through MW-assisted reduction under oxygen-free conditions. By leveraging the difference in standard reduction potentials, a Cu-rich Cu-Co alloy core was formed, surrounded by a shell consisting primarily of CoO, with minor phases of Co_xC and CuO.

Outstanding Performance in Methanol and Ethanol Oxidation: The optimal catalyst, CuCo_{2/1}, exhibited excellent performance in MOR and EOR, particularly for ethanol. Specifically, it reduced the applied potential by 155 mV for MOR and 197 mV for EOR at 50 mA·cm⁻², compared to OER. Furthermore, in a full-cell configuration, the ethanol-fed CuCo_{2/1}||Pt/C electrolyzer required 212 mV lower voltage than a conventional RuO₂||Pt/C OER to achieve 400 mA·cm⁻². Noteworthy, the use of ethanol as fuel for the production of hydrogen is directly correlated with one of the most challenging objectives of this thesis: to explore alternative anodic reactions for the OER (Obj. 3).

Economic and Technological Potential of AOR Systems: In addition to enhanced energy efficiency, the partial oxidation of alcohols produces formic acid and acetic acid, both of which are commercially valuable, thus offering improved economic return and system sustainability. These results collectively demonstrate that alcohol oxidation is a highly promising anodic alternative to OER, combining lower energy demands with product valorization and paving the way for more cost-effective and multifunctional electrochemical energy systems.

Scalability and Environmental Sensitivity: The current synthesis of Cu@CoO nanocatalysts requires strict oxygen-free conditions to avoid over-oxidation, which increases both production complexity and cost. Future research should focus on developing scalable and air-tolerant synthesis routes that can simplify fabrication and enhance industrial feasibility.

Particle Aggregation due to Ferromagnetism: The inherent ferromagnetic properties of cobalt can lead to nanoparticle aggregation during synthesis or operation, negatively impacting catalyst dispersion and stability. This issue may be addressed through interface engineering strategies or by incorporating surface-stabilizing agents.

Structural Instability during Long-term Operation: As described in **Chapter 4**, the CuCo_{2/1} catalyst gradually transforms into a CuO-CoO-CoOOH composite under prolonged electrochemical conditions. This irreversible oxidation results in performance degradation. A potential solution is entropy stabilization by introducing additional elements. Previous work by undergraduate researcher Ms. Gara Jimenez demonstrated that incorporating Ni and finely tuning the Cu:Co:Ni ratio in Cu_xCo_yNi_z systems can help identify optimal compositions with improved structural integrity and catalytic activity.

Faradaic Efficiency and Product Selectivity: For both methanol and ethanol oxidation reactions, the observed Faradaic efficiencies are below 100%, suggesting incomplete charge utilization and possible side reactions. This may be due to the formation of unquantified or insoluble gaseous byproducts such as CO or CO₂. Improving the catalyst's selectivity toward desirable oxidation products remains a critical step toward maximizing overall system efficiency.

5.3 General Outlook

Beyond the specific improvements required in each individual system, we also envision broader prospects for the overall work. Future studies should integrate advanced computational and characterization techniques to accelerate catalyst development and deepen mechanistic understanding.

Integration of advanced modeling and data-driven design: Future studies should incorporate DFT, artificial intelligence (AI), and machine learning (ML) to accelerate catalyst discovery and enable predictive understanding of reaction mechanisms. These approaches can help optimize composition, surface structure, and electronic configuration with higher efficiency.

In-situ/operando characterization: To gain real-time insights into catalyst behavior, advanced characterization techniques such as in situ Raman and infrared spectroscopy, synchrotron-based X-ray methods (operando XAS and XPS, February 2026, Soleil Synchrotron, Paris), and TEM should be employed. These tools can reveal structural evolution, intermediate species, and active sites during electrochemical operation.

Device-level optimization through MEA systems: While most evaluations in this work used three-electrode setups to probe intrinsic activity, future work should transition to MEA configurations to reflect practical conditions. Parameters such as ionic conductivity, electrolyte distribution, and interfacial resistance will play crucial roles in determining full-cell performance.

Integration with renewable energy sources: To align with future energy infrastructure, electrocatalytic systems should be engineered to couple efficiently with intermittent renewable energy inputs (e.g., solar, wind). Tolerance to variable current densities, startup/shutdown cycles, and temperature shifts will be key design considerations.

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Publications & patents

During the Ph.D

- ✚ **Xuesong Zhang**, et al. AuPt nanostructures with a high hydrogen evolution reaction activity through a halide-mediated microwave-assisted route. *J. Mater. Chem. A* (2025). (Q1, IF= 11.9, back cover)
- ✚ **Xuesong Zhang**, et al. Microwave-assisted synthesis of Cu/Co-based nanoheterostructures for high-efficiency alcohol oxidation. *Adv. Sci.* (2025). (Q1, IF= 14.1)
- ✚ Jesús Chacón-Borrero, **Xuesong Zhang**, et al. Enhanced lithium polysulfide adsorption and reaction with cobalt-doped spinel additives for robust lithium-sulfur batteries. *Energy Storage Mater.* (2025). (Q1, IF=18.9)
- ✚ Jesús Chacón-Borrero, **Xuesong Zhang**, et al. Ligand-mediated tailoring of self-supported Mn_xO_y@Ni(OH)₂ nanoheterostructures with enhanced OER performance. *ACS Appl. Mater. Interfaces.* 2025. (Q1, IF=8.2)
- ✚ Ren He, **Xuesong Zhang**, et al. Active site switching on high entropy phosphides as bifunctional oxygen electrocatalysts for rechargeable/robust Zn-air battery. *Energy &*

Environ. Sci. 2024. (Q1, IF=30.8)

Others

- ✚ **Xuesong Zhang**, et al. A novel $(\text{La}_{0.2}\text{Ce}_{0.2}\text{Gd}_{0.2}\text{Er}_{0.2}\text{Tm}_{0.2})_2(\text{WO}_4)_3$ high-entropy ceramic material for thermal neutron and gamma-ray shielding. *Mater. Des.* (2021). (Q1, IF=7.6)
- ✚ **Xuesong Zhang**, et al. $(\text{La}_{0.2}\text{Y}_{0.2}\text{Nd}_{0.2}\text{Gd}_{0.2}\text{Sr}_{0.2})\text{CrO}_3$: A novel conductive porous high-entropy ceramic synthesized by the sol-gel method. *J. Alloys Compd.* (2021). (Q1, IF=5.8)
- ✚ **Xuesong Zhang**, et al. Medical gamma-ray shielding performance of epoxy composite with lamellar ytterbium tungstate. *J. Rare Earths* (Chinese journal)
- ✚ Weijun Zhao, **Xuesong Zhang**, et al. A novel $(\text{La}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Gd}_{0.2}\text{Tm}_{0.2})_2\text{Zr}_2\text{O}_7$ high-entropy ceramic nanofiber with excellent thermal stability. *Ceram. Int.* (2021). (Q1, IF=5.1)
- ✚ Hao Zhang, **Xuesong Zhang**, et al. APD compressible aerogel-like monoliths with potential use in environmental remediation. *Materials* (2019). (Q2, IF= 3.1)

Patents

- ✚ First inventor: 2 Chinese patents on high-entropy materials synthesis
- ✚ Co-Inventor: 5 more Chinese patents on high-entropy materials and aerogels

Conferences, seminars, and summer schools

1. 8th Scientific Meeting of PhD Students (JPhD 2024), Bellaterra, Barcelona, Spain
27-29 November 2024
Poster presentation: AuPt nanostructures with a high hydrogen evolution reaction activity through a halide-mediated microwave-assisted route
2. Workshop on In Situ/Operando Characterization of Chemical and Electrochemical Energy Processes, ALBA Synchrotron, Barcelona, Spain
8 November 2024
Attendance
3. 7th Scientific Meeting of PhD Students (JPhD 2023), Bellaterra, Barcelona, Spain
7-9 June 2023
Oral presentation: Outperforming catalytic activity of $\text{Au}_x\text{Pt}_{1-x}$ nanostructures by a chlorine-assisted synthesis in hydrogen evolution reaction
4. The NaNaX10 2023 Conference, Vienna, Austria

3-7 July 2023

Poster presentation: Outperforming catalytic activity of $\text{Au}_x\text{Pt}_{1-x}$ nanostructures by a chlorine-assisted synthesis in hydrogen evolution reaction

5. The International Summer School on Sustainable Materials for Renewable Energy Applications (SURE2022), Bellaterra, Barcelona, Spain

11-15 July 2022

Attendance

6. 6th Scientific Meeting of BNC-b-PhD Students (JPhD 2021), Bellaterra, Barcelona, Spain
25-26 November 2021

Attendance

7. The First Advanced Ceramic Summit Forum, Changsha, Hunan, China
23-25 April 2021

Oral presentation: $(\text{La}_{0.2}\text{Ce}_{0.2}\text{Gd}_{0.2}\text{Er}_{0.2}\text{Tm}_{0.2})_2(\text{WO}_4)_3$ High-Entropy Ceramics for Thermal Neutron Absorption and Gamma-Ray Shielding

8. The 2020 Annual Academic Conference of the Chinese Society of Rare Earths & Jiangxi (Ganzhou) Conference on Green Development and Efficient Utilization of Rare Earth Resources, Ganzhou, Jiangxi, China
19-21 October 2020

Outstanding oral presentation: $(\text{La}_{0.2}\text{Y}_{0.2}\text{Nd}_{0.2}\text{Gd}_{0.2}\text{Sr}_{0.2})\text{CrO}_3$: A Novel Porous Conductive High-Entropy Ceramic Prepared by the Sol-Gel Method

Technical Expertise

-  **Synthesis:** Microwave-assisted, hydrothermal/solvothermal synthesis, sol-gel synthesis, solid-state synthesis, et al.
-  **Electrochemistry:** Three-electrode testing (CHI 760E, Bio-Logic), EIS, PEM/AEM electrolyzer fabrication.
-  **Characterization:** SEM, TEM, XRD, UV-vis, EPR, NMR, FT-IR, DLS, et al.
-  **Software:** OriginLab, CASAXPS, DigitalMicrograph3, Velox, Xpert HighScore, 3ds Max, et al.

Languages

-  **Chinese** (native)
-  **English** (fluent)

Publications

In this section, we include manuscripts already accepted by peer-reviewed scientific journals.

Publications Related to This Thesis

1. **Zhang, X.**, Chacón-Borrero, J., He, R., Gázquez, J., Torras, M., Cabot, A., Roig, A., Guardia, P.
AuPt Nanostructures with a High Hydrogen Evolution Reaction Activity through a Halide-mediated Microwave Assisted Route.
Journal of Materials Chemistry A, 2024. <https://doi.org/10.1039/d4ta04545a>
2. **Zhang, X.**, Gázquez, J., Pajares, A., Tonti, D., Guardia, P.
Microwave-assisted Synthesis of Cu/Co-based Nanoheterostructures for High-efficiency Alcohol Oxidation.
Advanced Science, 2025. <https://doi.org/10.1002/advs.202505581>

Other Publications during the Ph.D (Not Directly Related to This Thesis)

Characterization Contributions

3. Chacón-Borrero, J., Qi, X., **Zhang, X.**, et al.
Enhanced Lithium Polysulfide Adsorption and Reaction with Cobalt-doped Spinel Additives for Robust Lithium-sulfur Batteries
Energy Storage Materials, 2025, 104207. <https://doi.org/10.1016/j.ensm.2025.104207>
4. Chacón-Borrero, J., Martí-Sánchez, S., **Zhang, X.**, et al.
Ligand-mediated Tailoring of Self-supported $Mn_xO_y@Ni(OH)_2$ Nanoheterostructures with Enhanced OER Performance
ACS Applied Materials & Interfaces, 2025. <https://doi.org/10.1021/acsami.5c07315>

Data Analysis Contributions

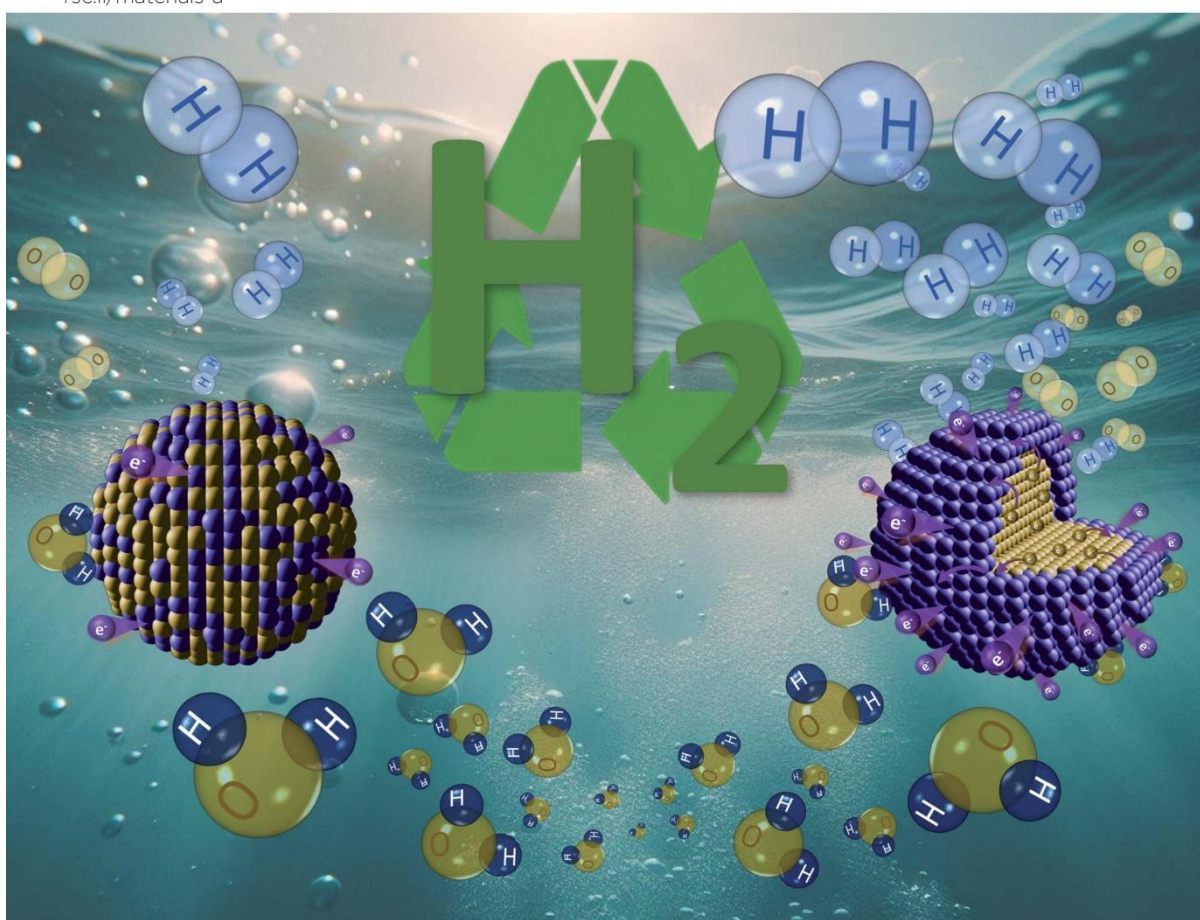
5. He, R., Wang, S., **Zhang, X.**, et al.
Active Site Switching on High Entropy Phosphides as Bifunctional Oxygen Electrocatalysts for Rechargeable/Robust Zn-air Battery
Energy & Environmental Science, 2024, 17 (19), 7193-7208. <https://doi.org/10.1039/d4ee01912a>

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AuPt nanostructures with a high hydrogen evolution reaction activity through a halide-mediated microwave assisted route†

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In light of the escalating scarcity and rising costs of platinum, it is imperative to take a strategic approach to its rational utilization as an electrocatalyst for the hydrogen evolution reaction (HER). In this study, we present a novel microwave (MW)-assisted synthesis route combined with the addition of halide ions, specifically chloride, for the synthesis of AuPt nanostructured electrocatalysts. By adjusting the Au : Pt ratio in solution, as well as the halide concentration, we achieve control over the composition, size, shape, and structure of the nanocrystals (NCs). Comparative analysis of the HER electrocatalytic activity revealed that samples produced in the presence of chloride exhibit reduced overpotentials and increased mass activities. Notably, when using a 1 : 4 Au : Pt ratio and 0.12 mmol of HCl, NCs display lower overpotential and Tafel slope values compared to commercial platinum carbon (Pt/C) catalyst (24 mV @ 10 mA cm⁻² and 13 mV dec⁻¹ compared to 31 mV @ 10 mA cm⁻² and 30 mV dec⁻¹ respectively). Moreover, this nanostructure exhibits a 6.9 fold higher mass activity compared to Pt/C (13.8 A mg_{Pt}⁻¹ and 2.0 A mg_{Pt}⁻¹, respectively). We attribute the enhancement in electrocatalytic performance to the formation of an Au-rich core supporting a Pt shell structure, which maximizes the exposure of Pt atoms. This synthesis route offers a pathway to produce Pt-based catalysts with superior electrocatalytic performance for HER, contributing to the rational use of Pt in green hydrogen production.

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1 Introduction

Compared to synthetic carbon-based fuels, hydrogen holds the potential for achieving carbon neutrality or even a negative carbon footprint throughout its life cycle.¹ Nevertheless, more than 90% of the world's hydrogen is produced from fossil fuels, predominantly *via* steam methane reforming, with only 4% generated through water electrolysis.^{2,3} Splitting water employing electrical current from renewable energy sources represents a zero CO₂ emission hydrogen production, commonly referred to as green hydrogen.⁴ The water-splitting process encompasses two half-reactions, the hydrogen evolution reaction (HER) at the cathode and the oxygen evolution reaction (OER) at the anode. To overcome the energy barrier of these electrochemical processes, voltages as high as 1.8 V may be required. In this scenario, electrocatalysts are key actors in lowering high overpotentials (η), enhancing efficiency, and reducing the total

energy consumption of hydrogen production.⁵ Consequently, the development of active, stable, and cost-effective electrocatalysts for water-splitting is critical for a green hydrogen-based economy.

Non-noble metal catalysts, such as metal-sulfides, -nitrides and -phosphides nanomaterials, have attracted significant attention in the past decade.^{6–8} Nevertheless, they exhibit lower stability and activity in water splitting compared to noble-metal catalysts (e.g. Pt, Ir or Ru).^{9–11} Indeed, Pt-based catalysts deliver high current densities at low overpotentials for HER.^{12–14} In that regard, despite their scarcity, the trade-off between the reduced energy consumption and the cost of Pt-based catalysts is considered advantageous. As such, the energy savings from lowering the cell operating voltage by 0.1 V can be up to ten times the cost of the Pt electrocatalyst.¹⁵

Multi-metallic nanocrystals (NCs) represent an appealing platform for developing low-Pt content catalysts providing unique physicochemical and catalytic properties resulting from the modulation of electronic states.^{16–20} For instance, bimetallic (PtRu, Pt₃Ni, PtNi, Pt₃Co or Pt₃Fe)^{21–23} or high entropy alloys (e.g., FeCoNiPtIr)^{24,25} have shown remarkable catalytic activity for low Pt loadings. In parallel, alternative strategies such as depositing a Pt atomic layer shell onto metallic cores,²⁶ single Pt atom decoration on carbon or metal oxides matrices,^{27,28} or the

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atomic Pt functionalization of porous structures^{29,30} have reported noteworthy progresses in this field.

Among multi-metallic structures, Au-based alloys have garnered much attention in the last decade with a plethora of well-established synthetic approaches.^{31,32} Despite the low binding energy and high overpotential of Au atoms for the HER,³³ alloyed electrocatalysts such as AuCu, AuPd, or AuNi have attracted interest due to their excellent activity combined with durability and low precious metal content.³⁴ In the particular case of AuPt alloys the combination of a Pt d-band shift with the proportional competencies of Au and Pt atoms has led to enhanced catalytic efficiency.³⁵ Moreover, Au stabilizes the Pt increasing the durability of AuPt catalysts by up to 30 times.³⁶

The combination of Au and Pt into a structure has been proven to provide significant advances in the activity and stability of electrocatalysts for acidic HER. On the one hand, controlling the stoichiometry in AuPt bimetallic alloys has an impact in reducing overpotentials as reported for Au₃Pt₈ NCs with $\eta = 26$ mV at 10 mA cm⁻².³⁷ On the other hand, Au–Pt heterostructures such as Au_{38,4}@Au_{9,3}Pt_{52,3} or Au@PtIr core-shell NCs have demonstrated also outstanding activities.^{38,39} In that direction, strain engineering in Au@PtCo_{0.05} core-shell structures has been reported to modulate the Pt d-band position.⁴⁰ Nowadays Au–Pt nanostructures are predominantly produced following two-step approaches (e.g. seed-mediated growth) thus increasing production costs while limiting mass production.³² Simultaneously, ultra-small AuPt NCs (below 3 nm) or the control over shape are highly desirable despite its compromised stability.⁴¹ Microwave (MW) assisted approaches have been successfully employed to produce metal or alloyed NCs but with limited control over the formation of complex structures such as dumbbell like or core-shell alloys.^{42,43} In that regard, halide ions have been identified as shape directors in the synthesis of metallic NCs,^{44–46} or as interphase mediators in the growth of semiconductor core-shell structures.^{47–49} Noteworthy, the effect of halide ions in the synthesis of alloys has received limited attention, particularly within the context of MW-assisted synthesis approaches.

Herein, we report on the MW-assisted synthesis of AuPt bimetallic NCs showing exceptional performance as electrocatalysts for the HER under acidic conditions. These NCs were produced by exposing a solution containing Au and Pt precursors to a MW radiation for 10 min. By adjusting the Au to Pt precursor molar ratio, various shapes, including spheres, clusters, and peanut-shaped NCs were synthesized. Interestingly, the controlled addition of halide ions in the reaction solution, such as chloride, provided further control over the shapes resulting in the formation of core-shell structures. The electrocatalytic activity for the HER in acidic media revealed a significant correlation between the Au to Pt feeding ratio or the presence of chloride. Noteworthy, despite the inherent lack of activity for HER of Au, the AuPt core-shell structures showed remarkable activities, surpassing those of commercial Pt/C. In particular, overpotentials as low as 24 mV @ 10 mA cm⁻² along with a mass activity up to 6.9 fold higher compared to that of commercial Pt/C. On the one hand, these results emphasize the

primary influence of chloride in modulating the reaction kinetics of Au and Pt, leading to the growth of an Au-rich core surrounded by a thin Pt shell. On the other hand, the presence of an Au core appears to be responsible for the enhanced catalytic activity of AuPt NCs compared to state-of-the-art Pt and Pt-based catalysts. To the best of our knowledge, this is the first work investigating the effect of chloride ions and Au : Pt feeding ratios as size and shape modulators in the MW-assisted synthesis of AuPt NCs, as well as their effect on the electrocatalytic activity.

2 Experimental

2.1 Materials

Tetrachloroauric(III) acid trihydrate (HAuCl₄·3H₂O, ≥99.9%), chloroplatinic acid hydrate (H₂PtCl₆·xH₂O, ≥99.9%), hydrochloric acid (HCl, 37%), polyvinylpyrrolidone (PVP_{10k}, *M*_w = 10 000), sodium borohydride (NaBH₄, 99%), Nafion 117 (~5% solution in a mixture of lower aliphatic alcohols and water) and 2-propanol (≥99.5%) were purchased from Sigma-Aldrich. Ethylene glycol (EG, ≥99%), ethanol and acetone were purchased from Panreac. Carbon black (Vulcan CX-72) was purchased from FuelCellStore. Commercial Pt/C (20 wt% on Vulcan) was purchased from Quintech. Sulfuric acid (H₂SO₄, 98%) was purchased from Fisher Chemical. All materials were used as received without further purification. Milli-Q water (18.2 MΩ cm, Milli-Q IQ, Merck Millipore) was employed for all experiments and solutions.

2.2 Synthesis of AuPt NCs

Samples were synthesized in a MW reactor (CEM Discover SP) operating at a frequency of 2.45 GHz and a power of 300 W. Solutions were placed inside the reactor and heated to the desired temperature by applying MW radiation. Temperature control was achieved by applying pulsed MW radiation. The samples produced by the MW-assisted approach were compared to those synthesized using a conventional oil-bath approach.

MW-assisted synthesis of AuPt nanocrystals. In a standard procedure for the synthesis of AuPt NCs, 25 mg of PVP_{10k} was placed in a 10 mL reaction tube and dissolved in 4 mL of ethylene glycol by continuous sonication (*ca.* 20 min). Next, 5.6 μL and 22.4 μL of 289 mM solutions of HAuCl₄·3H₂O and H₂PtCl₆·xH₂O, respectively, were added to the reaction tube resulting in a homogeneous yellowish-colored solution. The final metal ion concentration was 2 mM (Au and Pt). The tube was placed in the MW reactor and heated up to 160 °C (*ca.* 90 seconds). After 10 min at this temperature, the reaction tube was cooled down and 30 mL of acetone was added, followed by centrifugation at 6000 rpm for 10 min. The supernatant was discarded, and the solid precipitate dispersed in 1 mL of MQ-H₂O. The NCs were further washed by adding 10 mL of acetone to the solution and centrifuging it at 6000 rpm for 10 min. This washing procedure was repeated at least twice before dispersing the final sample into 1 mL of MQ-H₂O. According to the Au to Pt molar feeding ratio, the sample was labelled as AuPt_{1/4}.



Samples with different Au : Pt molar ratios were synthesized by following the above-described procedure but varying the volumes of the Au and Pt metal stock solutions added to the reaction solution. Regardless of the Au : Pt ratio, the total volume of the metal solutions (Au and Pt) was kept constant (28 μL) resulting in a 2 mM final metal ion concentration. Samples were labelled according to the Au : Pt feeding molar ratio: Pt(0 : 1), AuPt_{1/6}(1 : 6), AuPt_{1/4}(1 : 4), AuPt_{1/2}(1 : 2), AuPt_{1/1}(1 : 1), AuPt_{2/1}(2 : 1), AuPt_{4/1}(4 : 1), AuPt_{6/1}(6 : 1), and Au(1 : 0).

Halide-mediated synthesis of AuPt NCs. Following the above-described procedure, a given amount of chloride was introduced into the solution by adding a hydrochloric acid solution (HCl, 37 wt%). For instance, 10 μL (122 μmol of HCl) were added into a 4 mL of ethylene glycol solution containing 25 mg of PVP_{10k}, 5.6 μL of HAuCl₃·3H₂O solution (289 mM) and 22.4 μL of H₂PtCl₆·xH₂O solution (289 mM). The remaining procedures were identical to the ones described above, and these samples were labelled as AuPt_{1/4Cl}. Various samples (PtCl₃, AuPt_{1/6Cl}, AuPt_{1/4Cl}, AuPt_{1/2Cl}, AuPt_{1/1Cl}, AuPt_{2/1Cl}, AuPt_{4/1Cl}, AuPt_{6/1Cl}, AuCl₃) were produced by varying the Au : Pt ratios while keeping the HCl amount constant (0 : 1, 1 : 6, 1 : 4, 1 : 2, 1 : 1, 2 : 1, 4 : 1, 6 : 1, and 1 : 0, respectively).

Ligand removal. The above-produced NCs were coated by PVP molecules, forming an organic shell that may potentially interfere with the activity of the electrocatalysts. Therefore, PVP was removed from the surface of the AuPt NCs following a reported approach with minor modifications.⁵⁰ In a typical procedure, 10 mg of AuPt_{1/4Cl} NCs were dispersed by sonication in 20 mL of a NaBH₄/ethanol/H₂O solution (10 mg/10 mL/10 mL) for 3 min at room temperature. After sonication, 30 mL of ethanol were added to the mixture and NCs were collected by centrifugation (10 000 rpm, 20 min). The precipitate was then washed three times with ethanol and collected by centrifugation (10 000 rpm, 20 min) before being dried under ambient conditions and stored as a powder.

2.3 NCs characterization

The detail of characterizations of NCs are provided in ESI†

2.4 Electrochemical characterization

Catalyst preparation. The NCs produced were supported on carbon black to assess their electrocatalytic activity. Specifically, 4 mg of AuPt NCs and 32 mg of carbon black (1 : 8 weight ratio) were mixed in ethanol through continuous sonication for 3 h to ensure a uniform dispersion of AuPt NCs on carbon black. After drying the suspension under vacuum at 60 °C for 6 h, 4 mg of the catalysts (AuPt NCs and carbon black) were mixed with 1 mL of a solution containing 220 μL of MQ-H₂O, 750 μL of 2-propanol and 30 μL of Nafion. The mixture was then sonicated for 30 min until a homogeneous ink was formed.

Electrocatalytic performance. All electrochemical measurements were conducted at room temperature using a CHI760E electrochemical workstation (Shanghai Chenhua Instrument Co. Ltd., China). A standard three-electrode cell configuration with a glassy carbon (5 mm in diameter) and graphite electrodes as the working (WE) and counter (CE) electrodes, and an Ag/AgCl

electrode as the reference (RE) was used. The WE was prepared by polishing the surface before drop casting 5 μL of the AuPt NCs ink (see section above). The final Au and Pt metal loadings were determined by ICP-OES for each sample (see Table 1). Linear sweep voltammetry (LSV) was conducted at a scan rate of 5 mV s⁻¹ from 0 to -0.6 V (vs. Ag/AgCl) in a 0.5 M H₂SO₄ electrolyte. All potentials were corrected to the reversible hydrogen electrode (RHE) by following the Nernst equation: $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.0591\text{pH} + 0.197\text{ V}$. All the data were corrected for the 90% *iR* compensation within the cell. The electrochemical double-layer capacitance (C_{dl}) curves of the catalysts were measured by cyclic voltammetry (CV) in the non-faradaic region (0.397–0.497 V vs. RHE) at scan rates from 20 to 200 mV s⁻¹. The C_{dl} was calculated by following the equation: $C_{\text{dl}} = \Delta j / \nu$, where Δj ($\Delta j = (j_{\text{a}} - j_{\text{c}})/2$) and ν are the current density (at 0.447 V, mA cm⁻²) and scan rate (mV s⁻¹), respectively. From the C_{dl} , the electrochemical active surface area (ECSA) was calculated as: $\text{ECSA} = C_{\text{dl}}/C_s$, where the general specific capacitance (C_s) was 0.035 mF cm⁻² in 0.5 M H₂SO₄. Electrochemical impedance spectra (EIS) were acquired with an amplitude of 5 mV at frequencies ranging from 10⁶ to 0.01 Hz. The stability of catalysts was tested by running for 4000 cycles (accelerated scan rate 200 mV s⁻¹) at a potential amplitude between -0.05 and -0.15 V vs. RHE. Stability over time was evaluated by voltage-time plots keeping a constant current density of 10 mA cm⁻². Finally, the mass activity of the catalyst was calculated according to the following equations: $m_{\text{activity}} = j/m_{\text{Pt}}$ or $j/m_{\text{Au+Pt}}$, where j is the measured current density (mA cm⁻²) and m is the loading of Pt or Au + Pt inside the catalyst (*i.e.*, Pt/(Au + Pt) mg cm⁻²).

3 Results and discussion

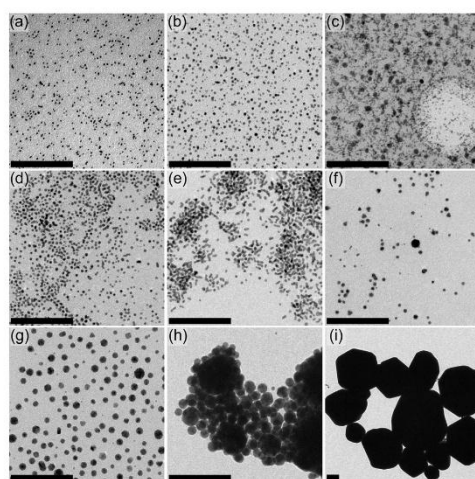
According to the literature, halide atoms have been explored in the synthesis of Au and Ag NCs as shape modulators.^{51,52} In this work, we went one step further and investigated the combined effect of chloride ions and Au : Pt feeding ratios as size and shape modulators in the MW-assisted synthesis of AuPt NCs.

First, we produced NCs at different Au : Pt ratios in the absence of chloride. As is reported in Fig. 1, the size and morphology of the NCs undergo a remarkable evolution as the Au : Pt molar ratio increases. For instance, at a 0 : 1 molar ratio, small Pt NCs (3 $\pm$ 1 nm) can be observed while large Au NCs (360 $\pm$ 80 nm) are produced with a 1 : 0 ratio (Fig. 1a and i). For ratios in between, the size of the NCs increases with an ascending Au : Pt ratio. This stresses out the different reaction kinetics for both metals. In terms of shape evolution, the NCs evolve from pseudo-spheres (Fig. 1b and c) or peanut-like (Fig. 1d and e) structures at lower Au concentrations, to faceted structures such as triangles (Fig. 1f) and hexagons (Fig. 1g–i) at higher Au content. Remarkably, samples produced with a 6 : 1 ratio exhibit large NCs surrounded by smaller ones, presenting a unique homogeneous morphology (Fig. 1h). According to this observation, tuning the Au : Pt molar ratios enables the modulation of size and shape of the NCs, likely due to the variations in the nucleation kinetics of Au and Pt. We then studied the time evolution of the NCs for a 1 : 1 molar ratio (Fig. S1†) observing a nucleation of small NCs already at the very beginning of the



Table 1 Summary of the structural composition and electrocatalytic performance at overpotentials @ 10 and 100 mA cm⁻², with Tafel slopes @ 10 mA cm⁻², for all the samples

Samples	Au : Pt feeding ratio	Au : Pt ICP-OES ratio	Overpotential at 10 mA cm ⁻² (mV)	Overpotential at 100 mA cm ⁻² (mV)	Tafel slope (mV dec ⁻¹)
Pt/C	0 : 1	0 : 1	31	72	30
Pt			28	66	19
Pt _{Cl}			29	101	33
AuPt _{1/6}	1 : 6	1 : 6.3	30	73	23
AuPt _{1/6Cl}		1 : 5.5	28	58	16
AuPt _{1/4}	1 : 4	1 : 3.2	32	81	26
AuPt _{1/4Cl}		1 : 1.6	24	51	13
AuPt _{1/2}	1 : 2	1 : 1.8	28	66	17
AuPt _{1/2Cl}		1 : 1.3	28	61	17
AuPt _{1/1}	1 : 1	1 : 0.7	31	102	33
AuPt _{1/1Cl}		1 : 0.8	39	126	47
AuPt _{2/1}	2 : 1	1 : 0.4	36	110	35
AuPt _{2/1Cl}		1 : 0.04	272	^b	248
AuPt _{4/1}	4 : 1	1 : 0.1	32	114	36
AuPt _{4/1Cl}		1 : 0 ^a	143	^b	191
AuPt _{6/1}	6 : 1	1 : 0.01	200	^b	146
AuPt _{6/1Cl}		1 : 0 ^a	360	^b	266
Au	1 : 0	1 : 0	311	^b	248
Au _{Cl}			390	^b	134

^a No Pt detection signal due to the limit of detection of ICP-OES equipment. ^b Current densities not achieved within the applied potential range.**Fig. 1** TEM images of AuPt NCs produced by a MW-assisted route at 160 °C adding different Au : Pt feeding molar ratios: (a) 0 : 1 – Pt, (b) 1 : 6 – AuPt_{1/6}, (c) 1 : 4 – AuPt_{1/4}, (d) 1 : 2 – AuPt_{1/2}, (e) 1 : 1 – AuPt_{1/1}, (f) 2 : 1 – AuPt_{2/1}, (g) 4 : 1 – AuPt_{4/1}, (h) 6 : 1 – AuPt_{6/1}, and (i) 1 : 0 – Au. Scale bar = 100 nm.

reaction which tend to aggregate after 10 min leading to worm or peanut-like shapes.

To elucidate the influence of other synthetic parameters such as the amount of PVP_{10k} or the metal ion concentration, experiments increasing the amount of these reactants were carried out. On the one hand, the influence of the PVP_{10k}

concentration in the reaction solution resulted in a varying trend depending on the Au : Pt ratio (Fig. S2†). For instance, at 1 : 0 and 0 : 1 ratios the size of the NCs remains constant despite the PVP_{10k} amount. In contrast, at intermediate ratios (1 : 4 and 1 : 1) the size of the NCs increases with increasing PVP_{10k} amount, showing a stronger effect at large Au : Pt ratios. On the other hand, when the total metal molar concentration was increased from 2 mM to 8 mM while keeping the PVP concentration constant the size of the NCs increased (Fig. S3†). For instance, for a 1 : 4 Au : Pt ratio, the size of the NCs evolve from a bimodal (5 ± 1 and 9 ± 1 nm NCs) to a monomodal distribution (6 ± 1 at 4 mM or 10 ± 2 nm) when the metal concentration (Au + Pt) was increased from 2 up to 8 mM respectively (Fig. S3a and c†). When the Au : Pt ratio was increased to 1 : 1, the NC size evolution follows a similar trend (Fig. S3d–f†). According to the above discussion, when the Au : Pt molar ratio is tuned the size can be effectively modulated from small (3 ± 1 nm at a 0 : 1 ratio) to rather large (360 ± 80 nm at 1 : 0 ratio) NCs. Conversely, the total metal molar concentration or the feeding amount of PVP_{10k} seem to have a lesser effect on the size and shape evolution.

Further characterization of the samples was carried out to elucidate the structure and composition of the AuPt NCs. For instance, XRD spectra revealed a shift in the [111] peak as the Au : Pt ratio increases (Fig. S4a†), which agrees with the increasing content of Au in a Pt structure. UV-vis spectra also demonstrated an evolution of the absorption with the increasing molar amount of Au. The deviation of the local surface plasmon resonance (LSPR) from its reported value for Au NCs (530 nm) is attributed to a size and composition evolution of the samples (Fig. S4b†).⁵³ For 2 : 1 and 4 : 1 ratio, this peak was located slightly below 530 nm which is consistent



with the presence of Pt atoms inside a Au NCs.⁵⁴ For higher Au concentrations (*i.e.*, 6 : 1 and 1 : 0), the red-shift of the LSPR was attributed to the presence of larger NCs.⁵⁵

After this initial analysis, AuPt NCs were produced following the same procedure as the previously presented samples, but with the addition of a controlled amount of chloride in the solution (Fig. 2). Despite this new set of NCs showed an increase in size with an increasing amount of Au too, the evolution of size and shape was remarkably different. For instance, from 0 : 1 to 1 : 2 ratios (Pt_{Cl} to AuPt_{1/2Cl}, Fig. 2a–d), shapes evolve from elongated or pod-like structures to nanoclusters with sizes ranging from 5 ± 1 to 14 ± 2 nm. These sizes are larger than those observed for NCs produced with the same Au : Pt ratio but without chloride (Fig. 1a–d). Noteworthy, we observed that samples synthesized in the presence of chloride resemble those produced without chloride but at higher Au : Pt ratios. For example, the samples produced at 1 : 2, 1 : 1, and 2 : 1 Au : Pt ratios in the presence of chloride (Fig. 2d–f, respectively) resemble those produced at 2 : 1, 4 : 1 and 6 : 1 without chloride (Fig. 1f–h, respectively). This observation suggests a modulation of the nucleation kinetics mediated by chloride, likely due to the different interaction or coordination of chloride with Au and Pt ions. This point will be discussed further below.

The final concentration of Au and Pt within the NCs was studied through ICP-OES analysis (Table 1 and Fig. S5†). For small Au : Pt feeding ratios, the stoichiometry of the NCs agree with the initial metal feeding ratios for samples produced without addition of chloride. Increasing the Au : Pt ratio up to 1 : 1 show a deviation of the stoichiometry of the NCs compared

to the feeding ratio but remain within reasonable agreement. However, for ratios above 1 : 1 the amount of Pt is smaller than the initial metal feeding. For instance, at 2 : 1 and 6 : 1 Au : Pt feeding ratios the, NCs stoichiometry is 1 : 0.4 and 1 : 0.01, respectively. In the presence of chloride this deviation trend between NC's stoichiometry and the feeding ratio appears to be clearly enhanced, in particular above the 1 : 1 ratio. Indeed, for 4 : 1 or 6 : 1 the values for Pt content are below the ICP-OES detection limit, thus indicating a decrease or delay in the Pt nucleation. From these data, we concluded that a high amount of Au strongly modulates Pt nucleation and growth kinetics, inhibiting its nucleation at large concentrations of Au (or low concentrations of Pt). This effect is enhanced when chloride was added to the reaction solution as the Au : Pt ratios of 2 : 1, 4 : 1, and 6 : 1 show a one-order-of-magnitude difference between samples produced with or without chloride. This led us to hypothesize the initial formation of chloride-stabilized metal clusters that modulate the reaction kinetics. To be specific, promoting the formation of more stable Pt clusters as compared to Au ones. This would delay nucleation favoring the reduction of Pt on top of an already-formed Au core when chloride is present in solution. Finally, the XRD peak positions evolves with increasing content of Au precursor (Fig. S4c†). The (111) peak position of the Pt structure (Pt_{Cl} sample) shifts to lower angles for sample AuPt_{1/6Cl} to AuPt_{1/1Cl}, thus indicating the possible formation of an AuPt alloy. Noteworthy, for higher Au content (AuPt_{2/1Cl}), the XRD peaks fit to an Au structure indicating the formation of an Au core. A similar trend was observed for the evolution of the LSPR (Fig. S4d†).

To investigate further the modulation by chloride in the nucleation-growth process, several volumes of a HCl solution (0, 10, 20 and 50 μ L) were introduced into a reaction solution containing different Au : Pt ratios (0 : 1, 1 : 4, 1 : 1 and 1 : 0, Fig. S6†). As a general trend, we observed that increasing chloride ions lead to an increase in the NCs size, which is consistent with a delayed or inhibited nucleation mediated by chloride-stabilized metal clusters (Fig. S6a–l†). However, when only Au was present in the solution, the size of the NCs decreased with increasing chloride concentration (Fig. S6m–q†). This highlights the opposite effect of chloride on both metal atoms; Au and Pt. In that context, adding chloride ions in the reaction solution likely promotes the formation of Au intermediates that favor nucleation against growth, thus leading to a controlled formation of NCs.⁵⁶ As for Pt, controlled conditions are likely already achieved without the addition of chloride. Consequently, an excess of chloride induces a delayed nucleation for Pt contributing to the formation of larger NCs or the reduction of Pt on top of the Au metal core. Overall, the differences in the final composition of NCs reported in Table 1 for samples produced under the same conditions but with varying chloride ion concentrations align with the above discussion. It is worth mentioning that the stabilization of metal clusters or complexes mediated by chloride is compatible with the reported etching effect of halides in metal NCs, particularly for Ag nanocubes.⁴⁹ This suggests the nucleation and dissolution of Pt atoms during the reaction, particularly on top of Au cores, which would

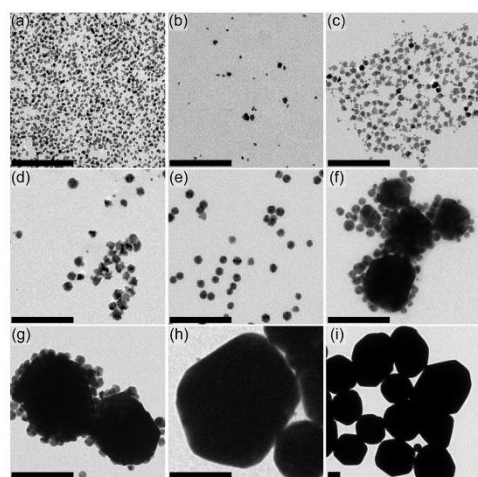


Fig. 2 TEM images showing the size and shape evolution of AuPt NCs produced by adding a controlled amount of chloride with different Au : Pt ratios: (a) 0 : 1 – Pt_{Cl}, (b) 1 : 6 – AuPt_{1/6Cl}, (c) 1 : 4 – AuPt_{1/4Cl}, (d) 1 : 2 – AuPt_{1/2Cl}, (e) 1 : 1 – AuPt_{1/1Cl}, (f) 2 : 1 – AuPt_{2/1Cl}, (g) 4 : 1 – AuPt_{4/1Cl}, (h) 6 : 1 – AuPt_{6/1Cl} and (i) 1 : 0 – Au_{Cl}. Scale bar = 100 nm.

explain the absence of Pt under certain conditions tested in this work.

We also conducted experiments to explore the influence of different amounts of PVP and increasing metal concentration at a fixed chloride concentration (Fig. S7 and S8†). Similar to the samples synthesized in the absence of chloride ions, excess of PVP has a strong influence in size and shape at higher Au concentrations (e.g., 1 : 1 and 1 : 0). In this regard, increasing amounts of PVP showed a stronger effect in the nucleation kinetics in the presence of chloride ions. In particular, a bimodal size distribution or bigger Au NCs were obtained at a 1 : 1 or 1 : 0 ratios, respectively (Fig. S7g–h†). This observation could be attributed to a potential interplay or competition between PVP and chloride ions, further modifying the reaction kinetics. The effect of increasing metal concentration is enhanced in the presence of additional chloride ions (Fig. S8†). In detail, an increasing concentration of metal ions in solution (from 2 mM to 4 or 8 mM) lead to a defocusing of the size distribution, observing a bimodal distribution where small NCs surround larger ones. This observation corroborates the strong correlation between the amount of chloride and the different nucleation kinetics for each metal. Finally, we sought to validate the influence of MW radiation on the experimental outcomes by comparing our samples with those produced under the same synthesis conditions but using conventional oil bath heating (Fig. S9†). For the 1 : 1 Au : Pt ratio, samples prepared both without and with the addition of chloride revealed significant disparities between both heating approaches. In particular, conventional oil bath heating resulted in larger NCs prone to nucleate in a bimodal size distribution. Finally, the benefits of the MW-assisted approach were confirmed by a high reproducibility and potential scalability (see Fig. S10†).

The electrocatalytic performance of the samples was tested by LSV measurements in an Ar-saturated aqueous solution (0.5 M H₂SO₄). Before running the LSV curves, the PVP_{10k} coating was removed to achieve the maximum availability of active sites on the surface.⁵⁷ PVP_{10k} removal was monitored by FT-IR measurements, confirming the absence of the three characteristic peaks for PVP_{10k} (1283 cm⁻¹ for C–N stretching; 1422 cm⁻¹ for C–H bending and 1656 cm⁻¹ for C=O stretching, Fig. S11†). As depicted in Fig. 3 and Table 1, samples synthesized under standard conditions generally show increasing overpotentials as the amount of Au increases in the NCs (Fig. 3a and b). Indeed, samples with the highest Au content (Au_{6/1} and Au_{1/0}) likely suffer from a higher hydrogen-adsorption-free energy associated with Au, resulting in poor activities.⁵⁸ When the amount of Pt increases inside the NCs, the overpotentials are similar to the one for commercial Pt/C catalyst (31 mV at 10 mA cm⁻²). For instance, samples produced with ratios ranging from 0 : 1 to 1 : 1 show overpotentials between 28 and 32 mV at 10 mA cm⁻². Nevertheless, at higher current densities up to 100 mA cm⁻², some of the AuPt samples exhibit lower or higher values (66 or 102 mV) than commercial Pt/C (72 mV). A similar trend is observed when analyzing the slope of the Tafel plots (Fig. 3c and Table 1). In particular, AuPt_{1/2}, AuPt_{1/4}, and AuPt_{1/6} samples display slopes of 17, 26, and 23 mV dec⁻¹, respectively, notably below that of commercial Pt/C (30 mV dec⁻¹). Overall,

when no additional chloride is added to the reaction solution, the highest performance is achieved for the AuPt_{1/2} sample, which owns a 1 : 1.8 Au : Pt ratio according to ICP-OES measurements (Table 1). Noteworthy, this result demonstrates that the activity is not directly related to the amount of Pt content.

The same electrochemical characterization was carried out for the set of samples produced in the presence of an excess of chloride ions (Fig. 3d–f). In this case, the evolution of the overpotentials as a function of the Pt content in the NCs shows a parabolic behavior, particularly for overpotentials measured at 100 mA cm⁻². Furthermore, within the composition range of 1 : 6 to 1 : 2 Au : Pt ratio, the electrocatalytic activity is enhanced compared to samples produced under standard conditions, without the addition of chloride. In that range, a clear minimum is observed for the AuPt_{1/4Cl} sample, which has a final Pt content of ca. 62% (1 : 1.63 Au : Pt ratio) and shows overpotentials of 24 and 51 mV at 10 and 100 mA cm⁻², respectively. It is worth mentioning that these values are below those measured for commercial Pt/C catalysts (31 and 72 mV at 10 and 100 mA cm⁻², respectively). Worth mentioning, the overpotentials are similar or even slightly higher when chloride is added for the rest of the samples. As discussed previously, the addition of chloride not only modifies the final Au : Pt content, but also promotes the formation of larger NCs. According to the general theory, larger NCs should lead to a lower activity due to the loss of active sites on the surface, as reflected in Pt and Pt_{Cl} samples (66 and 101 mV at 100 mA cm⁻², respectively). Nevertheless, when comparing samples produced with or without chloride in the range from 1 : 6 to 1 : 2 Au : Pt ratio, lower overpotentials are observed when chloride is added despite the larger NCs. The same effect is observed for the Tafel slopes (β), observing lower slopes in the same range (i.e., 1 : 6 to 1 : 2 Au : Pt ratio) when NCs were produced using an excess of chloride. Even more interestingly, the AuPt_{1/4Cl} sample demonstrates the best electrocatalytic activity towards HER despite having a lower Pt content than AuPt_{1/6Cl}. Notably, the AuPt_{1/4Cl} and AuPt_{1/2} ratios are closely aligned (1 : 1.63 and 1 : 1.76, respectively). However, their respective performance disparities highlight that catalytic activity is not solely determined by Pt content. A straightforward comparison of the reported values for the Tafel slope and overpotentials in the literature highlights the outstanding performance observed for our AuPt_{1/4Cl} NCs (Fig. 3g). Finally, the performances measured for Pt and Pt_{Cl} samples were similar to the values measured for a commercial Pt/C catalyst.

Regarding the enhancement of electrocatalytic activities, the observed improvement after the addition of chloride is likely attributed to the formation of a Au–Pt structure rather than a simple AuPt alloy. This structure appears to provide higher Pt exposure to the environment. To explore this hypothesis, HR-STEM and EDX mapping were performed on both AuPt_{1/4} and AuPt_{1/4Cl} samples (Fig. 4). Noteworthy, HR-HAADF images of AuPt_{1/4} NCs exhibit a homogeneous crystallinity, indicating an even distribution of Au and Pt atoms along the NCs (as seen in Fig. 4a). In addition, EDX mapping confirms that the Pt signal is slightly higher than that of Au in all the AuPt NCs, as shown in



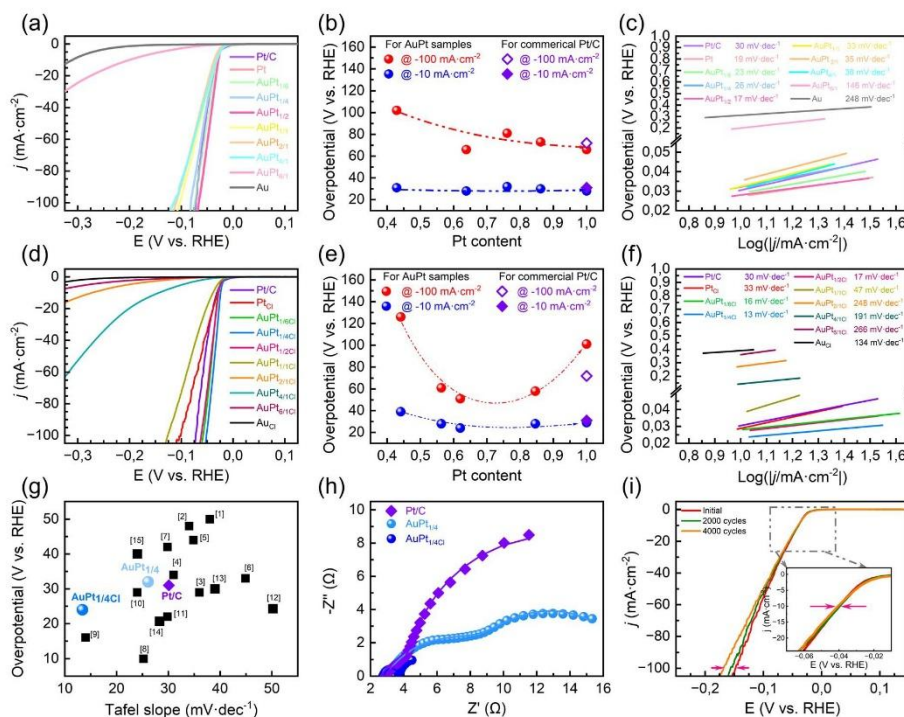


Fig. 3 Electrocatalytic HER performance in 0.5 M H_2SO_4 . (a) LSV, (b) overpotentials vs. Pt content, and (c) Tafel slope of the AuPt NCs synthesized in the absence of chloride, respectively. (d) LSV, (e) overpotentials vs. Pt content, and (f) Tafel slope of the set of AuPt NCs synthesized in the presence of chloride, respectively. (g) Overpotential vs. Tafel slope plot for commercial Pt/C, AuPt_{1/4}, and AuPt_{1/4Cl} samples. Data are compared with reported values of state-of-the-art electrocatalysts based on Pt alloys (references are listed in Table S1†). (h) EIS Nyquist plot for commercial Pt/C, AuPt_{1/4}, and AuPt_{1/4Cl}. (i) Evolution of the stability of AuPt_{1/4Cl} by running CV for 2000 and 4000 cycles, respectively.

Fig. 4b, consistent with the Au : Pt ratio measured by ICP-OES (1 : 3.19, as detailed in Table 1). In contrast, HR-HAADF images acquired from AuPt_{1/4Cl} NCs reveal a non-homogeneous contrast, particularly noticeable as blurred contrast in the core of the NC, as shown in Fig. 4c. Elemental EDX mapping further illustrates a core-shell structure wherein a Pt shell surrounds an Au core (Fig. 4d). This observation corroborates the influence of chloride in modulating the Au and Pt nucleation/growth kinetics, favoring the nucleation of the Au core while limiting the nucleation of Pt atoms onto its surface. Some works have featured the selective binding of halide ions to different metals and the formation of various metal complexes and clusters with different reaction kinetics.⁵⁹ This could elucidate preferential nucleation and subsequent stabilization of Au cores over Pt ones. This hypothesis is further supported by the observation of a lower Pt content in AuPt_{1/4Cl} compared to AuPt_{1/4} (1 : 1.63 and 1 : 3.19 respectively, Table 1). Accordingly, the higher efficiency of AuPt_{1/4Cl} is unequivocally attributed to a rational distribution of the Pt atoms on the Au core's surface. This configuration not only maximizes the exposure of Pt atoms

to the environment but also prevents Au atoms from interacting with the environment, thereby reducing the contribution of low-performing Au atoms to HER. Despite that, it is essential to note that this should not impede the contribution of the electron cloud of the Au core to the electrocatalytic activity pointing towards a synergetic effect. However, this hypothesis requires further investigation beyond the scope of this work.

The calculation of the electrochemical active surface area (ECSA) of the three samples (Pt/C, AuPt_{1/4}, and AuPt_{1/4Cl}) by applying CV curves at different scan rates in the non-faradaic region (Fig. 5a) demonstrates that the core-shell heterostructure maximizes the available active Pt atoms. According to the slopes, commercial Pt/C exhibits the highest slope (1.46 mF cm⁻²), while AuPt_{1/4} and AuPt_{1/4Cl} show lower slope values (0.42 and 1.18 mF cm⁻², respectively) resulting in higher ECSA for Pt/C (41.7 m² g⁻¹) compared to AuPt_{1/4} and AuPt_{1/4Cl} (12.0 and 33.7 m² g⁻¹, respectively). The commercial Pt/C catalyst contains a 20 wt% Pt content, whereas AuPt_{1/4} and AuPt_{1/4Cl} have 8.4 and 6.9 wt% Pt content. Despite the higher number of active sites for commercial Pt/C compared to AuPt samples, its overpotential is



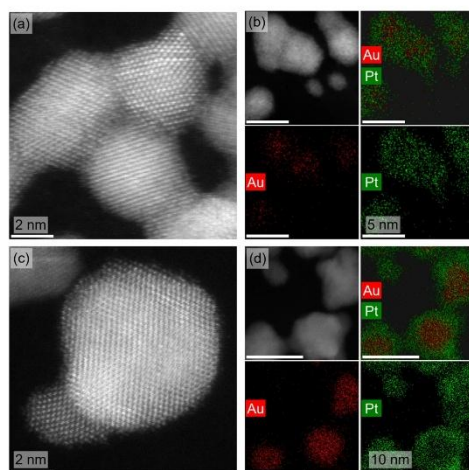


Fig. 4 High-resolution HAADF-STEM images and EDX elemental mapping of AuPt_{1/4} (a and b) and AuPt_{1/4Cl} (c and d). Au and Pt elements are displayed as red and green colours, respectively.

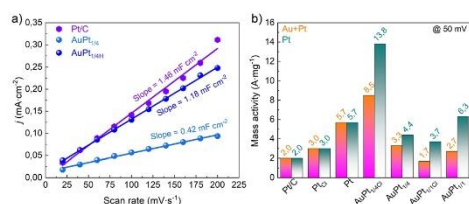


Fig. 5 (a) Calculation of the electrochemical double layer capacitance (C_{dl}) for commercial Pt/C, AuPt_{1/4}, and AuPt_{1/4Cl} (see Fig. S15†) (b) mass activities of commercial Pt/C, AuPt_{1/4}, AuPt_{1/4Cl}, and AuPt_{1/4Cl} at the overpotential of 50 mV with the same total loading on the working electrode.

still higher so indicating that the activity is not only related to the ECSA but other parameters promoting the reaction. To further analyze the intrinsic activity of these electrocatalysts, their mass activity (normalized by the Pt mass) was calculated at 50 mV (Fig. 5b). Noteworthy, the mass activity of the AuPt_{1/4Cl} is 13.8 A mg_{Pt}^{−1}, which is almost 6.9 times higher than that of commercial Pt/C (2.0 A mg_{Pt}^{−1}), and around 3.1 times of AuPt_{1/4} (4.4 A mg_{Pt}^{−1}). Therefore, arranging Pt atoms on top of a Au core likely enhances its activity while promoting interactions with the core that significantly improved the overall HER electrocatalytic performance. Certainly, when considering the total mass of the NCs (Au + Pt) these values are slightly low. For instance, 8.5 A mg^{−1} for the AuPt_{1/4Cl} sample (Fig. 5b) which represents a 4.25 fold enhancement compared to Pt/C.

To gain a better insight into the kinetic mechanism governing the HER, EIS characterization was performed on

commercial Pt/C, AuPt_{1/4}, and AuPt_{1/4Cl} samples (Fig. 3h and S13†). The estimated solution resistance (R_s) observed from the Nyquist plots is similar for all samples and in the order of 2.8 to 2.9 Ω at −13 mV (Table S2†). In this case, the semicircles can be attributed to two interfaces associated with the adsorption of species (mainly H⁺, first semicircle R_1) and the electron transfer (second semicircle R_2).⁶⁰ When comparing the R_1 values for the three samples, the AuPt_{1/4Cl} shows the lowest value (0.87 Ω) compared to the values for AuPt_{1/4} and commercial Pt/C (6.34 and 1.54 Ω , respectively). By comparing the resistance corresponding to the transfer of electrons (R_2), AuPt_{1/4Cl} shows again the lowest values (2.4 Ω) compared to the ones measured for AuPt_{1/4} and Pt/C (9.24 and 17.04 Ω , respectively). This indicates efficient species adsorption and rapid charge transfer in AuPt_{1/4Cl}. To corroborate our hypothesis, we ran HER measurements in neutral (1 M potassium phosphate-buffered saline, PBS, pH = 7) and alkaline (1 M potassium hydroxide, pH = 14) media. As shown in Fig. S14,† in neutral and alkaline solutions, AuPt_{1/4} and AuPt_{1/4Cl} exhibited poorer performance than commercial Pt/C. Remarkably, AuPt_{1/4Cl} exhibits the highest overpotential at 10 mA cm^{−2} in alkaline media, while AuPt_{1/4} showed a better activity close to the one measured for commercial Pt/C (Table S3†). This observation proves the crucial role of H⁺ adsorption in the HER performance of AuPt structures and, at the same time, the synergetic effect differences that Au and Pt could play in alkaline media. The significant improvement of the AuPt_{1/4} NCs from neutral to alkaline media could result from the higher adsorption energy of H⁺ species in Au, thus leading to an improved activity at higher pH.

Finally, the stability of the AuPt_{1/4Cl} electrocatalyst was evaluated by conducting 2000 and 4000 cycles of CV (Fig. 3i) and a chronopotentiometry test (Fig. S16†). As observed, the overpotential at 10 mA cm^{−2} does not undergo significant increases, remaining close to 30 mV after 2000 or even 4000 cycles, as shown in the inset image of Fig. 3i. A slight deviation is observed in the overpotentials at 100 mA cm^{−2}, with an increase from 148 mV to 156 mV and 168 mV for 2000 and 4000 cycles, respectively. Nevertheless, the activity of the AuPt_{1/4Cl} electrocatalyst remains relatively stable after 4000 cycles. The chronoamperometry test was carried out by drop casting a catalyst ink containing AuPt_{1/4Cl} NCs onto a carbon cloth (1 × 1.25 cm²). Chronopotentiometry was run over 200 hours in an H-type cell maintaining a constant current density of 10 mA cm^{−2} (Fig. S16†). Samples show rather good stability with an increase of the overpotential of ca. 5–6% after 200 hours. These results are consistent with the trend observed in Fig. 3i and comparable with the reported stabilities for other catalyst (Table S4†), indicating a good stability of AuPt_{1/4Cl} performance over prolonged operating time. Analysis of the sample after the long stability test confirmed that the structure of a Au-rich core surrounded by a Pt shell was preserved (Fig. S17†). Noteworthy, X-ray photoelectron spectroscopy (XPS) analysis confirmed a partial oxidation of the Pt-shell as well as an increase in the Au³⁺ contribution after 200 hours (Fig. S18†). This increase could be related to a partial migration of Au atoms to the surface that eventually does reduce the catalytic activity. Indeed, this hypothesis is in line with the ca. 25% increase of the



overpotential after 12 hours when the current was increased to 50 mA cm⁻² (Fig. S16†).

4 Conclusions

In summary, we have successfully synthesized a series of AuPt NCs with varying Au:Pt ratios using a fast and facile MW-assisted synthetic approach. The addition of HCl played a pivotal role providing precise control over the structure and morphology of the NCs. Ultimately, AuPt_{1/4}Cl was identified as the most promising candidate for the HER in acidic media demonstrating remarkable electrocatalytic activity despite not having the highest Pt content among all the samples. Precisely, it exhibited overpotentials of 24 mV and 51 mV (at 10 and 100 mA cm⁻², respectively) and a Tafel slope of 13 mV dec⁻¹. This excellent performance can be attributed to the distinctive core-shell structure of NCs, wherein a Pt shell wraps the Au core. This configuration maximizes the exposure of Pt atoms to the surrounding environment, surpassing the activity of commercial Pt/C catalysts. Furthermore, synergistic effects between the Au core and the Pt shell likely contribute to superior performance by modulating the electronic structure of the core-shell nanocatalyst. Despite its low Pt content, the AuPt_{1/4}Cl nanocatalyst exhibited a hydrogen production rate significantly higher than that of commercial Pt/C (by 4.25 fold) and surpassed the AuPt_{1/4} counterpart (by 2.6 fold). In this context, the low Pt content combined with the high hydrogen production rate offsets the presence of Au in the NCs. Future research should focus on replacing Au with more cost-effective and abundant elements such as Ag, Ni, Co, or Cu. These findings underscore the successful integration of MW-assisted synthesis and halide ions for the rational design of low-Pt content electrocatalysts with enhanced performance in HER.

Data availability

The data supporting this article have been included as part of the ESI†

Author contributions

Xuesong Zhang: conceptualization, data curation, formal analysis, investigation, methodology, writing-original draft, writing-review & editing. Jesús Chacón-Borrero: data curation, formal analysis, investigation. Ren He: formal analysis, investigation. Jaume Gázquez: formal analysis, methodology. Miquel Torres: conceptualization, investigation. Andreu Cabot: conceptualization, writing-review & editing. Anna Roig: funding acquisition, investigation, writing-review & editing. Pablo Guardia: conceptualization, data curation, formal analysis, funding acquisition, investigation, methodology, project administration, supervision, writing-original draft, writing-review & editing.

Conflicts of interest

The authors declare no conflict of interest.

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References

- 1 F. Ueckerdt, C. Bauer, A. Dirnau, J. Everall, R. Sacchi and G. Luderer, *Nat. Clim. Change*, 2021, **11**(5), 384–393.
- 2 P. Nikolaidis and A. Poullikkas, *Renew. Sustain. Energy Rev.*, 2017, **67**, 597–611.
- 3 C. Xu, M. Zhang, X. Yin, Q. Gao, S. Jiang, J. Cheng, X. Kong, B. Liu and H. Q. Peng, *J. Mater. Chem. A*, 2023, **11**, 18502–18529.
- 4 M. Chatenet, B. G. Pollet, D. R. Dekel, F. Dionigi, J. Deseure, P. Millet, R. D. Braatz, M. Z. Bazant, M. Eikerling, I. Staffell, P. Balcombe, Y. Shao-Horn and H. Schäfer, *Chem. Soc. Rev.*, 2022, **51**, 4583–4762.
- 5 Y. Luo, Z. Zhang, M. Chhowalla and B. Liu, *Adv. Mater.*, 2022, **34**, 1–18.
- 6 W. A. Saidi, T. Nandi and T. Yang, *Electrochem. Sci. Adv.*, 2023, **3**, e2100224.
- 7 S. Pan, H. Li, D. Liu, R. Huang, X. Pan, D. Ren, J. Li, M. Shakouri, Q. Zhang, M. Wang, C. Wei, L. Mai, B. Zhang, Y. Zhao, Z. Wang, M. Graetzel and X. Zhang, *Nat. Commun.*, 2022, **13**, 2294.
- 8 J. Zhao, N. Liao and J. Luo, *J. Mater. Chem. A*, 2023, **11**, 9682–9690.
- 9 F. Liu, C. Shi, X. Guo, Z. He, L. Pan, Z. Huang, X. Zhang and J. Zou, *Adv. Sci.*, 2022, **9**, 2200307.
- 10 M. Herbaut, M. Sijaj and J. P. Claverie, *ACS Appl. Nano Mater.*, 2021, **4**, 907–910.
- 11 L. Jiao and H. L. Jiang, *Chin. J. Catal.*, 2023, **45**, 1–5.
- 12 Y. Li, Y. Sun, Y. Qin, W. Zhang, L. Wang, M. Luo, H. Yang and S. Guo, *Adv. Energy Mater.*, 2020, **10**, 1–20.
- 13 I. T. McCrum and M. T. M. Koper, *Nat. Energy*, 2020, **5**, 891–899.
- 14 S. Zhu, X. Qin, F. Xiao, S. Yang, Y. Xu, Z. Tan, J. Li, J. Yan, Q. Chen, M. Chen and M. Shao, *Nat. Catal.*, 2021, **4**, 711–718.
- 15 J. Tymoczko, F. Calle-Vallejo, W. Schuhmann and A. S. Bandarenka, *Nat. Commun.*, 2016, **7**, 10990.
- 16 Y. Nakaya and S. Furukawa, *Chem. Rev.*, 2023, **123**, 5859–5947.



- 17 J. Liu, C. Lee, Y. Hu, Z. Liang, R. Ji, X. Y. D. Soo, Q. Zhu and Q. Yan, *SmartMat*, 2023, **4**, e1210.
- 18 Y. Shi, Z. R. Ma, Y. Y. Xiao, Y. C. Yin, W. M. Huang, Z. C. Huang, Y. Z. Zheng, F. Y. Mu, R. Huang, G. Y. Shi, Y. Y. Sun, X. H. Xia and W. Chen, *Nat. Commun.*, 2021, **12**(1), 1–11.
- 19 Z. Zeng, S. Kuang, Z. F. Huang, X. Chen, Y. Su, Y. Wang, S. Zhang and X. Ma, *Chem. Eng. J.*, 2022, **433**, 134446.
- 20 R. Q. Yao, Y. T. Zhou, H. Shi, W. Bin Wan, Q. H. Zhang, L. Gu, Y. F. Zhu, Z. Wen, X. Y. Lang and Q. Jiang, *Adv. Funct. Mater.*, 2021, **31**, 2009613.
- 21 D. Strmcnik, M. Uchimura, C. Wang, R. Subbaraman, N. Danilovic, D. Van Der Vliet, A. P. Paulikas, V. R. Stamenkovic and N. M. Markovic, *Nat. Chem.*, 2013, **5**(4), 300–306.
- 22 C. Lim, A. R. Fairhurst, B. J. Ransom, D. Haering and V. R. Stamenkovic, *ACS Catal.*, 2023, **13**, 14874–14893.
- 23 N. S. Porter, H. Wu, Z. Quan and J. Fang, *Acc. Chem. Res.*, 2013, **46**, 1867–1877.
- 24 G. Gao, G. Zhu, X. Chen, Z. Sun and A. Cabot, *ACS Nano*, 2023, **17**, 20804–20824.
- 25 Y. Lu, K. Huang, X. Cao, L. Zhang, T. Wang, D. Peng, B. Zhang, Z. Liu, J. Wu, Y. Zhang, C. Chen and Y. Huang, *Adv. Funct. Mater.*, 2022, **32**, 2110645.
- 26 S. Deng, B. Zhang, P. Choo, P. J. M. Smeets and T. W. Odom, *Nano Lett.*, 2021, **21**, 1523–1529.
- 27 Y. Chen, H. Sun, B. C. Gates, Y. Chen, H. Sun and B. C. Gates, *Small*, 2021, **17**, 2004665.
- 28 K. L. Zhou, Z. Wang, C. B. Han, X. Ke, C. Wang, Y. Jin, Q. Zhang, J. Liu, H. Wang and H. Yan, *Nat. Commun.*, 2021, **12**(1), 1–10.
- 29 W. Geng, X. Song, Z. Wei, M. Cao and R. Cao, *ACS Appl. Energy Mater.*, 2022, **5**, 15597–15604.
- 30 Z. X. Ge, Y. Ding, T. J. Wang, F. Shi, P. J. Jin, P. Chen, B. He, S. B. Yin and Y. Chen, *J. Energy Chem.*, 2023, **77**, 209–216.
- 31 K. Loza, M. Heggen and M. Epple, *Adv. Funct. Mater.*, 2020, **30**, 1909260.
- 32 P. Lu, J. Zhou, Y. Hu, J. Yin, Y. Wang, J. Yu, Y. Ma, Z. Zhu, Z. Zeng and Z. Fan, *J. Mater. Chem. A*, 2021, **9**, 19025–19053.
- 33 D. Strmcnik, P. P. Lopes, B. Genorio, V. R. Stamenkovic and N. M. Markovic, *Nano Energy*, 2016, **29**, 29–36.
- 34 S. Tanaka, N. Hoshi and M. Nakamura, *ChemElectroChem*, 2023, **10**, e202300095.
- 35 D. Mott, J. Luo, P. N. Njoki, Y. Lin, L. Wang and C. J. Zhong, *Catal. Today*, 2007, **122**, 378–385.
- 36 P. P. Lopes, D. Li, H. Lv, C. Wang, D. Tripkovic, Y. Zhu, R. Schimmenti, H. Daimon, Y. Kang, J. Snyder, N. Becknell, K. L. More, D. Strmcnik, N. M. Markovic, M. Mavrikakis and V. R. Stamenkovic, *Nat. Mater.*, 2020, **19**, 1207–1214.
- 37 Y. Yu, S. J. Lee, J. Theerthagiri, Y. Lee and M. Y. Choi, *Appl. Catal., B*, 2022, **316**, 121603.
- 38 Y. Cao, Y. Xiahou, L. Xing, X. Zhang, H. Li, C. S. Wu and H. Xia, *Nanoscale*, 2020, **12**, 20456–20466.
- 39 X. Wang, J. Qi, X. Luo, Z. Yang, Y. Fan, Z. Jiang, C. Liu, J. Yang and W. Chen, *Int. J. Hydrogen Energy*, 2021, **46**, 36771–36780.
- 40 R. Wan, M. Luo, J. Wen, S. Liu, X. Kang and Y. Tian, *J. Energy Chem.*, 2022, **69**, 44–53.
- 41 L. D. Germano, V. S. Marangoni, N. V. V. Mogili, L. Seixas and C. M. Maroneze, *ACS Appl. Mater. Interfaces*, 2019, **11**, 5661–5667.
- 42 M. Torras and A. Roig, *ACS Omega*, 2020, **5**, 5731–5738.
- 43 M. Torras and A. Roig, *Cryst. Growth Des.*, 2021, **21**, 5027–5035.
- 44 J. Seth and B. L. V. Prasad, *Nano Res.*, 2016, **9**, 2007–2017.
- 45 X. Huang, Y. Li, Y. Li, H. Zhou, X. Duan and Y. Huang, *Nano Lett.*, 2012, **12**, 4265–4270.
- 46 S. E. Lohse, N. D. Burrows, L. Scarabelli, L. M. Liz-Marzán and C. J. Murphy, *Chem. Mater.*, 2014, **26**, 34–43.
- 47 P. Guardia, S. Nitti, M. E. Materia, G. Pugliese, N. Yaacoub, J. M. Greneche, C. Lefevre, L. Manna and T. Pellegrino, *J. Mater. Chem. B*, 2017, **5**, 4587–4594.
- 48 J. Lim, W. K. Bae, K. U. Park, L. Z. Borg, R. Zentel, S. Lee and K. Char, *Chem. Mater.*, 2013, **25**, 1443–1449.
- 49 S. Ghosh and L. Manna, *Chem. Rev.*, 2018, **118**, 7804–7864.
- 50 X. Zhang, B. Liu, C. Hu, S. Chen, X. Liu, J. Liu, F. Chen, J. Chen and F. Xie, *Spectrochim. Acta, Part A*, 2020, **228**, 117733.
- 51 P. C. Chen, M. Liu, J. S. Du, B. Meckes, S. Wang, H. Lin, V. P. Dravid, C. Wolverton and C. A. Mirkin, *Science*, 2019, **363**, 959–964.
- 52 Q. Wang, W. Jia, B. Liu, W. Zhao, C. Li, J. Zhang and G. Xu, *Chem.-Asian J.*, 2012, **7**, 2258–2267.
- 53 V. Coviello, D. Forrer and V. Amendola, *ChemPhysChem*, 2022, **23**, e202200136.
- 54 V. Amendola, R. Pilot, M. Frascioni, O. M. Maragò and M. A. Iati, *J. Phys.: Condens. Matter*, 2017, **29**, 203002.
- 55 J. Rodríguez-Fernández, J. Pérez-Juste, F. J. G. De Abajo and L. M. Liz-Marzán, *Langmuir*, 2006, **22**, 7007–7010.
- 56 A. Loiudice and R. Buonsanti, *Nat. Synth.*, 2022, **1**(5), 344–351.
- 57 Q. Fan, K. Liu, Z. Liu, H. Liu, L. Zhang, P. Zhong, C. Gao, Q. Fan, K. Liu, Z. Liu, H. Liu, L. Zhang, P. Zhong and C. Gao, *Part. Part. Syst. Character.*, 2017, **34**, 1700075.
- 58 Z. W. She, J. Kibsgaard, C. F. Dickens, I. Chorkendorff, J. K. Nørskov and T. F. Jaramillo, *Science*, 2017, **355**, eaad4998.
- 59 J. Choi, Y. Lee, J. Kim and H. Lee, *J. Power Sources*, 2016, **307**, 883–890.
- 60 Y. Guo, B. Hou, X. Cui, X. Liu, X. Tong and N. Yang, *Adv. Energy Mater.*, 2022, **12**, 2201548.





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Microwave-Assisted Synthesis of Cu/Co-Based Nanoheterostructures for High-Efficiency Alcohol Oxidation

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Hybrid water splitting, using methanol or ethanol oxidation reactions (MOR and EOR) at the counter electrode during electrochemical hydrogen generation, offers an efficient alternative to the sluggish oxygen evolution reaction (OER). This study reports Cu/Co-based core-shell nanocrystals (NCs) showing excellent performance for both MOR and EOR. The structure, composition and size of the NCs can be controlled by adjusting the synthesis parameters in a one-pot microwave-assisted process. The electrocatalytic performance of the NCs shows lower potentials for both MOR and EOR compared to the OER. They consist of a copper-rich metallic core initially encapsulated by a shell composed of cobalt oxide and cobalt carbide. This nanoheterostructure evolves to a copper oxide core surrounded by an oxide shell consisting of small cobalt- and copper-oxide nanodomains upon chronopotentiometry experiments. The excellent performance in both MOR and EOR is attributed to the oxidation of the NCs and a concomitant diffusion process that forms small oxide clusters. The final structure provided NCs with high mass activities for both alcohol oxidation reactions, producing formic and acetic acid as products (for MOR and EOR, respectively). Finally, the NCs are tested for hybrid water electrolysis, demonstrating high hydrogen production along with high stability.

energy barrier, limiting the kinetics of water's overall splitting.^[3,4] To circumvent this issue, the sluggish OER can be replaced by a thermodynamically more favorable oxidation reaction, the so-called hybrid water electrolysis.^[5,6]

Molecules such as alcohols, amines, urea, hydrazine, or carbohydrates have been studied intensively as excellent candidates for cost-efficient and environmentally friendly production of hydrogen.^[7–9] Among them, methanol and ethanol stand out as excellent fuels for hybrid water electrolysis and direct alcohol fuel cells due to their high energy densities (17.3 and 22.7 MJ·L^{−1}, respectively), ease of fuel handling, and low cost.^[10,11] Both methanol and ethanol oxidation reactions (MOR and EOR, respectively) have been extensively studied to identify oxidation pathways that can lead to the total or partial oxidation of alcohol. While complete oxidation of both alcohols delivers the highest current densities (6 and 12 electrons for MOR and EOR, respectively), it also produces CO₂, which increases the carbon footprint of the overall

hydrogen production. In contrast, the partial oxidation of methanol or ethanol allows for the concomitant production of hydrogen and value-added molecules under zero carbon footprints. In particular, formic acid follows the CO-free oxidation pathway in the MOR, and acetic acid follows the C2 pathway in the EOR.^[12] In this context, ethanol emerges as a superior candidate for sustainable hydrogen production compared to methanol, owing to its higher energy density, lower toxicity, and renewable production from biomass.^[13]

During hybrid water splitting, the applied voltages must remain below the required for the OER, thereby constraining the operating current densities and subsequently reducing the overall electrochemical efficiency.^[14,15] This reduction in the current density is largely offset by the simultaneous production of hydrogen and value-added molecules with zero CO₂ emissions. For instance, by exploiting the electro-oxidation of organic compounds, Yu et al. reduced the energy costs in ≈14.3%.^[16] Nevertheless, the electrocatalytic performance still requires improvements to achieve industrially viable Faradaic efficiencies and to attain current densities at a moderate applied potential. For the MOR, but particularly for the EOR, this is achieved by noble metal (Pt- or Pd-) and nickel-based catalysts, which raises additional environmental and economic concerns.^[17–19] For instance, Qin

1. Introduction

Electrochemical water splitting is widely acknowledged as one of the most environmentally friendly processes to produce green hydrogen, especially when powered by renewable energy sources.^[1,2] Nevertheless, the multiple electron transfer for the oxygen evolution reaction (OER) at the anode leads to a large

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et al. synthesized PtRuNiCoFeGaPbW high entropy alloy ultrathin nanowires to oxidate methanol to CO_2 .^[20] In these circumstances, transition metal-based NCs (Cu, Co, and Ni) have been identified as potential electrocatalysts for alcohol oxidation reactions, offering an environmentally friendly and economically sustainable hydrogen production.^[21]

For instance, Cu-based materials show a high affinity to adsorb methanol and hence high activity for the MOR on Cu-based NCs has been reported.^[22] Simultaneously, cobalt-based catalysts have attracted much attention for their excellent performance in water splitting, in particular for the OER and MOR.^[19,23,24] Interestingly, cobalt doping in Ni-, Pt- and Pd-based catalysts results in an enhancement of the catalytic activity.^[25,26]

The combination of copper and cobalt in a NC has garnered significant attention due to the enhancement of the catalytic activity. Recently, various Cu-Co nanomaterials, such as Cu@CoO_x ,^[27] CuCo_2O_4 ,^[28] copper cobalt phosphides,^[29] copper cobalt selenide,^[30] copper cobalt layered double hydroxide,^[31] boron-copper cobalt oxides,^[32] copper cobalt hydroxycarbonates,^[33] or copper cobalt sulfide,^[34] have been reported.

The formation of Mott-Schottky heterostructures has shown promising results in improving the intrinsic conductivity of oxide semiconductors.^[35] This approach induces interface effects in catalysts, such as electronic coupling, charge transfer and defects, and optimizing the heterostructure's intermediate adsorption/desorption behavior.^[36] The increased active site availability results in a superior electrocatalytic performance. Moreover, exploiting the Mott-Schottky heterojunction interface between metal and semiconductor can significantly enhance semiconductor Fermi level management, utilizing Schottky barriers to achieve rectifying effects and confining semiconductor hole or electron states, thereby significantly improving electrocatalytic performance.^[37] Additionally, transition metal carbides are potential alternatives to platinum-based catalysts, leveraging their platinum-like electronic structures. Furthermore, synthesizing highly dispersed carbides as core nanoparticles supports synergistic enhancements.^[38] Recent literature underscores that synthesizing Mott-Schottky heterostructures typically involves multistep syntheses, rendering them complex and time-consuming.^[36,39–41] Hence, there is an urgent need to explore a more rapid and streamlined synthesis route.

In this work, we report a one-pot microwave (MW)-assisted synthesis for producing Cu/Co-based nanoheterostructures. These heterostructures, consisting of a metal core surrounded by a metal-oxide/metal-carbide shell, are embedded or self-supported on a metal-oxide sheet. Adjusting the feeding molar ratio between the copper and cobalt precursors provides control over the compositions of the core/shell NCs and the morphology of supporting metal-oxide nanosheets. For instance, an excess of cobalt precursor leads to the formation of a CuCo alloy at the core and cobalt carbide and cobalt oxide domains at the shell. Under an applied potential, the structure evolves due to the diffusion and partial oxidation of atoms, resulting in an oxidized core surrounded by small Cu- and Co-oxide domains. This process boosts the formation of Mott-Schottky heterojunctions along the structure, providing high electrocatalytic performance for both MOR and EOR. The nanoheterostructures were tested for hybrid water splitting, showing high stability under moderate current densi-

ties and the production of value-added products such as formic or acetic acid.

2. Results and Discussion

2.1. Synthesis and Characterization of Cu/Co NCs

Self-supported Cu/Co NCs were produced by a novel MW-assisted synthesis route developed in this work. In particular, different molar ratios of copper- and cobalt-acetylacetonates (i.e., Cu:Co ranging from 1:4 to 4:1) were mixed in a benzyl alcohol solution containing PVP_{3.5k}. In all the experiments, the total metal concentration in the solution was kept constant at 17.5 mM. After MW radiation, nanoheterostructures consisting of NCs (regions with higher electron density) formed on top of thin substrates (areas of lower electron density) were observed (Figure 1). Despite these nanoheterostructures varied in size according to the Cu:Co ratio, we could not identify a clear trend allowing us for a precise size control. Nevertheless, nanoheterostructures produced at 1:4 and 4:1 molar ratios show the largest cores (Figure 1a,e, respectively). According to the XRD results, all samples showed peaks consistent with the Fm-3m(225) structure of $\text{Cu}_{0.48}\text{Co}_{0.52}$ (JCPDS #50-1452). However, for the [111] and [200] peaks, we observed a deviation that was accentuated, in particular, for $\text{CuCo}_{1/4}$ and $\text{CuCo}_{1/2}$ samples, with peaks shifting toward higher angles as cobalt content increased (Figure S1, Supporting Information). This is consistent with the differences between the [111] peak for copper (43.297°, JCPDS #04-0836) and cobalt (44.216°, JCPDS #15-0806). Additionally, the presence of a broad peak at $\approx 61^\circ$ and a small peak at 41.5° for the $\text{CuCo}_{1/4}$ sample suggested the presence of copper or cobalt oxides. These results are compatible with the formation of a metallic Cu_xCo_y core, self-supported by a copper- and/or cobalt oxide shell.

According to the literature, the formation of a metallic core was unexpected, as similar conditions led to the formation of metal oxides.^[42] Control experiments were carried out by adding only one of the metal precursors (1:0 and 0:1), leading to the formation of Cu_2O and CoO NCs (Figure S2, Supporting Information). This observation indicates that neither the PVP_{3.5k}, benzyl alcohol, nor the purging of the tube with Ar, did provide enough reductive conditions to produce metallic NCs. Nonetheless, it is worth noticing that the synthesis conditions promote the reduction of copper precursor from Cu^{2+} to Cu^+ , resulting in the formation of a Cu_2O phase. Thus, the formation of a metallic core would result from a redox synergy reaction between copper and cobalt complexes under these conditions as has been reported for instance for CuNi NCs.^[43] Further characterization confirmed that a Cu-rich metallic core is formed in all the samples while cobalt is distributed between the core and the shell (see discussion below).

To further understand the formation of the Cu/Co NCs, the final stoichiometry of the samples was analyzed by ICP-OES (Figure S3, Supporting Information). According to the results, we systematically observed a slightly higher copper content compared to the initial Cu:Co feeding ratios. For instance, the final copper contents for $\text{CuCo}_{1/4}$ (20.0%), $\text{CuCo}_{1/2}$ (33.3%), $\text{CuCo}_{1/1}$ (50.0%), $\text{CuCo}_{2/1}$ (66.6%) and $\text{CuCo}_{4/1}$ (80.0%) were 23.1, 36.2, 55.8, 71.3 and 82.0%, respectively.

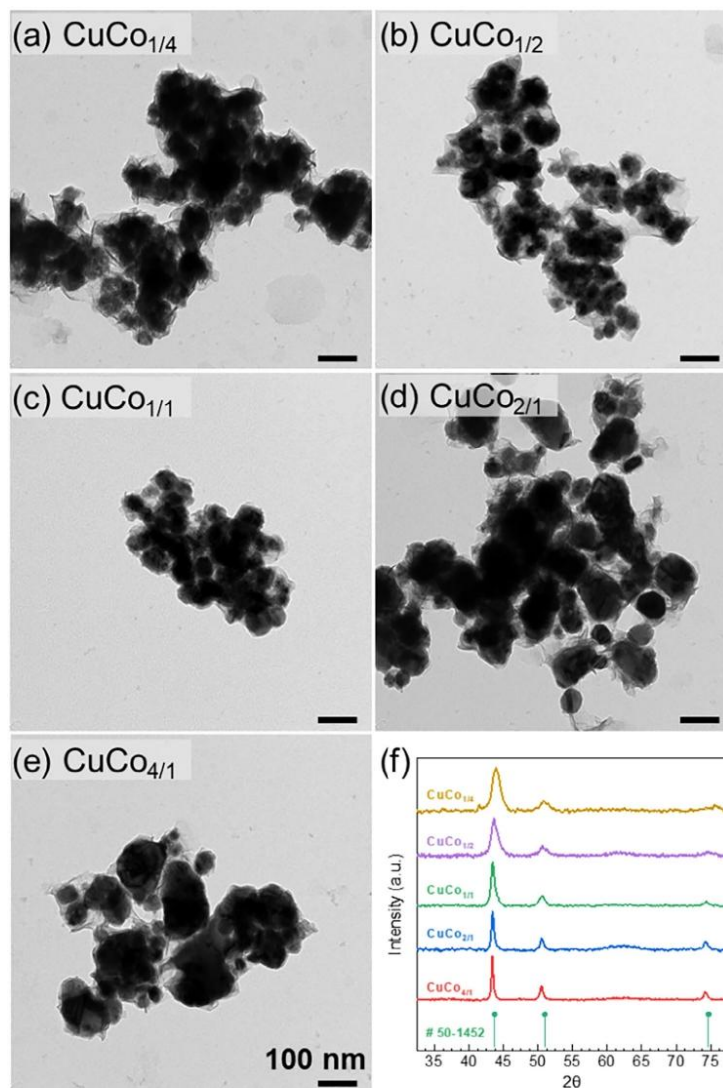


Figure 1. TEM images of Cu/Co NCs produced by a MW-assisted route at 200 °C adding different Cu:Co feeding molar ratios: a) 1:4 – CuCo_{1/4}, b) 1:2 – CuCo_{1/2}, c) 1:1 – CuCo_{1/1}, d) 2:1 – CuCo_{2/1}, e) 4:1 – CuCo_{4/1}, f) XRD patterns of Cu/Co NCs along with the reference for Cu_{0.48}Co_{0.52} alloy (JCPDS: #50-1452). All the scale bars correspond to 100 nm.

2.2. Electrocatalytic Characterization of Cu/Co NCs

The electrocatalytic performances of the Cu/Co NCs for the OER, MOR and EOR were evaluated at room temperature using a conventional three-electrode system. Samples produced at

0:1 and 1:0 ratios (labeled as CoO and Cu₂O, respectively) were also tested for a consistent analysis. All the measurements were carried out in a 1 M KOH electrolyte (OER), where methanol or ethanol (0.5 M) was added for the MOR and EOR (see Experimental Section for details). The summary of the CV polar-

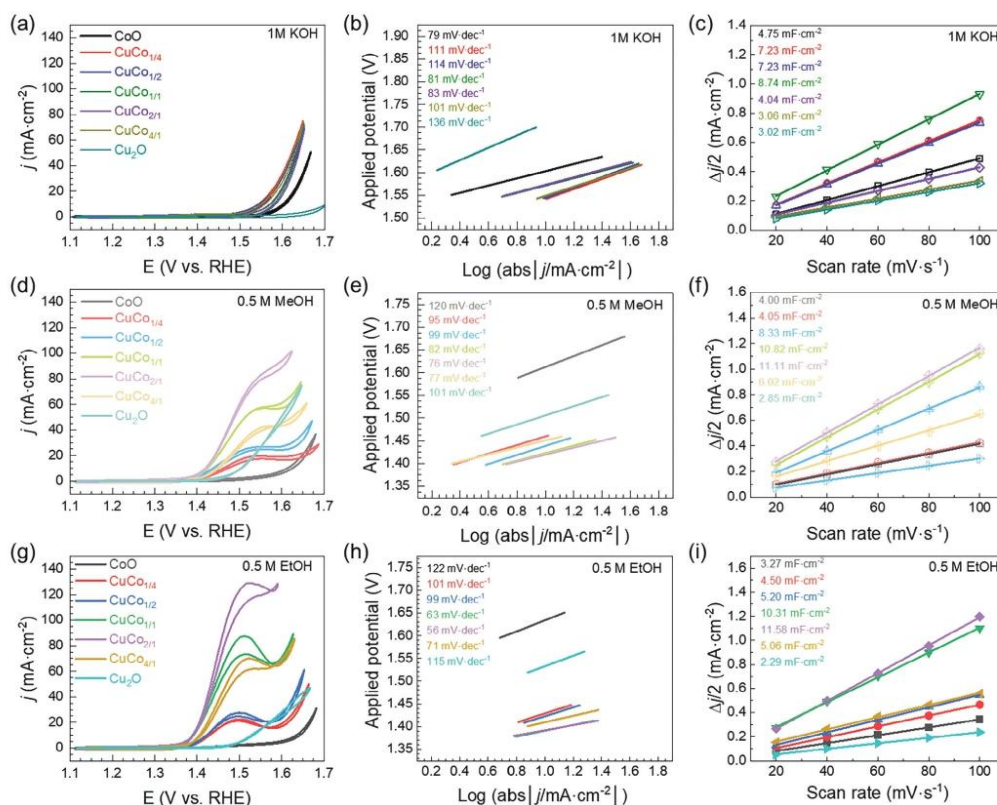


Figure 2. CV curves, Tafel and C_{dl} plots for all Cu/Co NCs samples measured in a-c) 1 M KOH – OER; d-f) in 1 M KOH + 0.5 M methanol – MOR and g-i) in 1 M KOH + 0.5 M ethanol – EOR. Measurements were carried out by drop-casting 5 μ L of the catalyst ink in a glassy carbon electrode (WE). All potentials were corrected to the RHE and 90% of iR compensation. Note that Tafel plots (b, e and h) were plotted as a function of the applied potential.

ization curves along with Tafel and C_{dl} plots are reported in Figure 2.

2.2.1. Cu/Co NCs Performance for the OER

Cu_2O and CoO samples show the lowest OER activity among all samples (Figure 2a-c). In particular, the Cu_2O exhibited an onset potential above 1.60 V and overpotentials of 470 mV at 10 $\text{mA}\cdot\text{cm}^{-2}$, the highest Tafel slope (136 $\text{mV}\cdot\text{dec}^{-1}$) and the lowest C_{dl} value (3.02 $\text{mF}\cdot\text{cm}^{-2}$). This performance obtained for the copper oxide NCs is consistent with previously published studies.^[44] CoO NCs' performance slightly improves with a lower overpotential (370 mV at 10 $\text{mA}\cdot\text{cm}^{-2}$) and lower Tafel slope (79 $\text{mV}\cdot\text{dec}^{-1}$). Yet, those values were still high compared to the substantial improvement in OER activity observed for Cu/Co NCs prepared with both copper and cobalt, where curves practically overlap for all samples. A closer look revealed that the

Cu/Co nanoheterostructures produced at the highest cobalt contents showed the best performances ($\text{CuCo}_{1/4}$ and $\text{CuCo}_{1/2}$), with $\text{CuCo}_{1/2}$ achieving the lowest overpotentials (310 and 390 mV at 10 and 50 $\text{mA}\cdot\text{cm}^{-2}$, respectively). For comparison, the $\text{CuCo}_{2/1}$ sample showed slightly higher overpotentials (340 and 410 mV at 10 and 50 $\text{mA}\cdot\text{cm}^{-2}$, respectively). This suggests that increasing cobalt content enhances the OER efficiency, which is in good agreement with the superior OER performance of CoO relative to Cu_2O alone. Despite the significant improvement of the Cu/Co NCs compared to the metal-oxide NCs, these values remain comparable to those thus far reported in the literature for similar bimetallic nanoparticles.^[45,46]

2.2.2. Cu/Co NCs Performance for the MOR

The addition of methanol to the electrolyte (0.5 M) resulted in a significant modification of the polarization curves (Figure 2d-f).

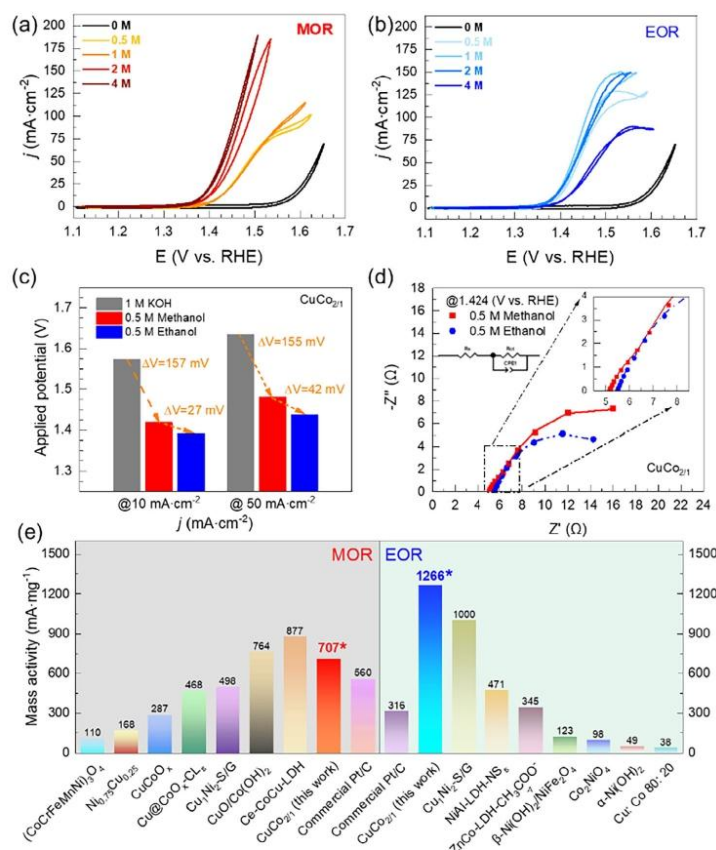


Figure 3. CV curves for the MOR a) and EOR b) at different methanol or ethanol concentrations (0, 0.5, 1, 2, 4 M). c) comparison of the potentials applied for CuCo_{2/1} NCs to reach 10 and 50 mA cm⁻² in the OER, MOR, EOR. d) EIS for the CuCo_{2/1} in a KOH electrolyte containing 0.5 M methanol (red squares) or 0.5 M ethanol (blue circles). e) the comparison of mass activity for CuCo_{2/1} with the state of art for MOR and EOR based on transition metal-based materials and commercial Pt/C (for references see Figure S6, Tables S1 and S2, Supporting Information).

On one hand, the presence of methanol clearly improved the activity for the Cu₂O NCs, displaying an onset potential at 1.46 V, an applied potential of 1.50 V at 10 mA cm⁻², and a reduced Tafel slope (101 mV dec⁻¹). Conversely, CoO NCs showed lower performance in the presence of methanol, as evidenced by higher overpotentials and steeper Tafel slopes than those measured for the OER. On the other hand, also in this case in all the Cu/Co NCs the performances improved with respect to the metal-oxide NCs, exhibiting lower onset potentials (below 1.40 V vs RHE) and lower required potentials, along with a notable oxidation peak observed at ≈1.54 V versus RHE, characteristic of the occurrence of the MOR. According to the CV curves, activity increased with the increasing amount of copper in the NCs, reaching a peak performance for the CuCo_{2/1} sample. This sample showed the lowest applied potentials (1.42 and 1.48 V at 10 and 50 mA cm⁻², respec-

tively) and lower Tafel slope (76 mV dec⁻¹), along with the highest oxidation peak current density (81.45 mA cm⁻² at 1.55 V vs RHE) and the largest ECSA (277.75 cm² mg⁻¹). This trend was opposite to the one observed for the OER where performances improved with increasing content of Co. Remarkably, the CuCo_{1/1} sample showed similar performance as the CuCo_{2/1} at lower potentials, though its performance decay as the potential increases, delivering lower current densities (1.42 and 1.51 V vs RHE at 10 and 50 mA cm⁻², respectively, Figure 2d).

Following the preliminary analysis, we studied the effect of the methanol concentration on the electrocatalytic performance of the CuCo_{2/1} NCs. CV curves were recorded at different methanol concentrations (0, 0.5, 1, 2, 4 M, Figure 3a). Results showed a significant decrease in onset potential as the methanol concentration increased. At the same time, the oxidation peak at ≈1.54 V

versus RHE gradually vanished, shifting from 1.55 to 1.40 V versus RHE. This observation clearly indicates an optimal methanol concentration for our experimental set-up, where a trade-off between the oxidation and diffusion rates is accomplished at the WE interface. At low concentrations, the reaction kinetics is likely limited by the diffusion of methanol molecules to the electrode surface. Instead, at higher concentrations, the methanol concentration and the oxidation products likely saturate the electrode's surface, thus decreasing the activity and, hence, the intensity of the oxidation peak.

2.2.3. Cu/Co NCs Performance for the EOR

Finally, samples were tested for the EOR by adding 0.5 M ethanol into the electrolyte. Compared to methanol, ethanol is a non-toxic compound that can be produced from biomass or agricultural feedstocks as well as waste. However, it has been well-established that the presence of a higher carbon content results in lower oxidation efficiency.^[18] Indeed, we observed higher potentials at 10 mA•cm⁻² for both oxides during the EOR (1.52 and 1.63 V at 10 mA•cm⁻² for Cu₂O and CoO, respectively) compared to the ones for MOR (1.46 and 1.61 V at 10 mA•cm⁻² for Cu₂O and CoO, respectively). Certainly, this difference was particularly pronounced in the Cu₂O sample, which exhibited higher values than the CoO. This indicates that cobalt demonstrates superior performance compared to copper, in contrast with the better performance of Cu₂O for the MOR.

When analyzing the EOR activity of the Cu/Co NCs, all samples exhibited lower onset potentials compared to Cu₂O and CoO, reflecting a similar trend to that observed for the MOR. The electrooxidation activity increased as the content of copper in the NCs increased, reaching its maximum for CuCo_{2/1} NCs. In particular, this sample showed an onset potential of 1.37 V along with required potentials as low as 1.39 and 1.44 V to reach current densities of 10 and 50 mA•cm⁻², respectively. Noteworthy, these values are even lower than those measured for the same sample but for the MOR (e.g., potentials of 1.42 and 1.48 V at 10 and 50 mA•cm⁻², respectively). Moreover, we observed that the ethanol oxidation peak was more pronounced, taking place at a lower voltage, and delivering higher current densities (i.e., 108.02 mA•cm⁻² at 1.50 V vs RHE for the EOR, compared to 81.45 mA•cm⁻² at 1.55 V vs RHE for MOR). These values clearly surpass those observed for the MOR and the OER, unequivocally identifying the CuCo_{2/1} NCs as a superior catalyst for the EOR. Indeed, we observed that at equal applied voltages, all NCs delivered higher current densities for the EOR compared with the MOR, underlining the effectiveness of these particular nanoheterostructures in catalyzing ethanol oxidation.

Similar to the MOR, we studied the effect of ethanol concentration by increasing the concentration from 0.5 to 4 M (Figure 3b). We observed a clear activity enhancement as the concentration increased to 1 M. However, further increasing the concentration of ethanol did not result in an increase in activity. Indeed, at a 4 M ethanol concentration, the current density decreased by almost a factor of 1.5 at high voltages (above ca. 1.45 V). This trend suggests the presence of intermediates that remain strongly absorbed by the active sites, reducing ECSA and thereby diminishing efficiency. For instance, an increasing production rate of

acetic acid would eventually lead to a local increase of its concentration at the WE interface, displacing the equilibrium and hence decreasing the kinetic of the reaction.

2.2.4. Comparison of the electrocatalytic performance for Cu/Co NCs

For a straightforward comparison of the OER, MOR, and EOR performance, we focused on the CuCo_{2/1} and compared the applied potentials at 10 and 50 mA•cm⁻². For instance, at 10 mA•cm⁻², the applied potentials for the EOR and the MOR were 157 and 184 mV lower compared to the OER. When the current density increased to 50 mA•cm⁻², the gap between the OER and MOR potentials was kept relatively constant (155 mV), whereas that for the EOR further increased to 197 mV. Likewise, the difference between MOR and EOR performances increased from 27 at 10 mA•cm⁻² to 42 mV at 50 mA•cm⁻². The EIS plots for MOR and EOR revealed that the solution resistance (R_s) was comparable (Figure 3d; Table S3, Supporting Information) for both reactions, with MOR exhibiting similar R_s (5.14 Ω compared to 5.48 Ω for EOR). Additionally, the charge transfer resistance (R_{ct}) for ethanol oxidation (11.73 Ω) was lower than that for methanol oxidation (16.78 Ω), indicating that CuCo_{2/1} has a lower overall resistance, providing a faster kinetics for ethanol oxidation, which is in agreement with the observed higher activity for the EOR.

Finally, the mass activities of the CuCo_{2/1} NCs and commercial Pt/C for the MOR and EOR at 50 mA•cm⁻² were directly compared using the same experimental set-up along with the data reported in the literature for transition metal-based catalysts (Figure 3e). For the MOR, CuCo_{2/1} NCs exhibited slightly higher mass activities compared to commercial Pt/C (707 against 560 mA•mg⁻¹) and comparable to recently reported values on cobalt–copper layer double hydroxide and CuO/Co(OH)₂ nanosheets (877 mA•mg⁻¹ and 764 mA•mg⁻¹, respectively).^[31,47] Notably, commercial Pt/C exhibits a peak at low applied voltages (0.78 V vs RHE, Figure S6, Supporting Information). However, the relatively low magnitude of this peak significantly limits its overall catalytic activity, as increasing the voltage beyond this point leads to a decline in current density. On the other hand, CuCo_{2/1} NCs exhibited a rather high mass activity for EOR (1266 mA•mg⁻¹), which is significantly higher compared to similar reported works for Cu₂Ni₂S₂G (1000 mA•mg⁻¹)^[48] or commercial Pt/C catalyst (316 mA•mg⁻¹). Hence, CuCo_{2/1} NCs showed remarkable mass activities for both alcohol oxidation reactions, similar to or outperforming state-of-the-art Cu-Co-based catalysts. This observation is of particular interest as best performing catalysts for MOR typically do not show high activities for EOR, and vice versa. Overall, CuCo_{2/1} NCs exhibited dual catalytic activity for both ethanol and methanol oxidation, demonstrating exceptional high performance in the more challenging EOR. These findings prompted a more in-depth characterization of CuCo_{2/1} NCs to investigate the origin of this enhanced performance.

2.3. Characterizations of CuCo_{2/1} NCs

The structure of the CuCo_{2/1} NCs was further elucidated through XPS analysis (Figure 4a–d; Figure S7, Supporting Information). Deconvolution of the C1s high-resolution spectrum revealed five

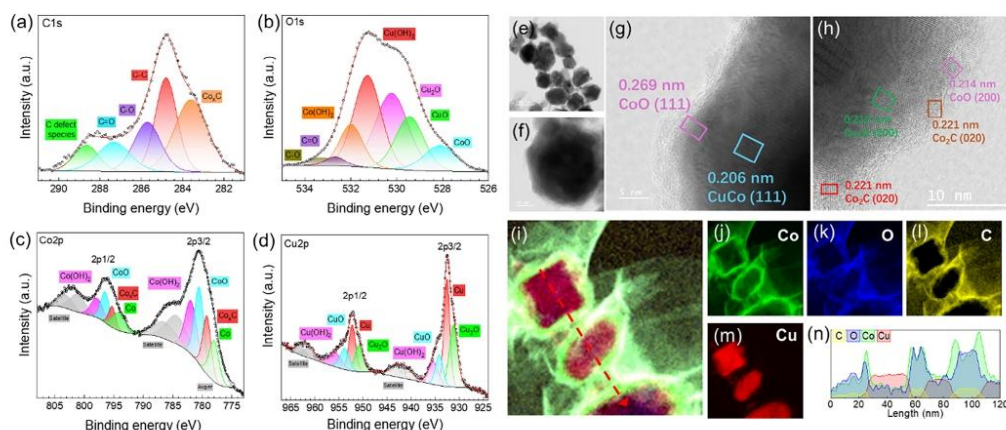


Figure 4. a) C1s, b) O1s, c) Co2p, and d) Cu2p XPS high-resolution spectra of $\text{CuCo}_{2/1}$. e, f) Low magnification and g, h) HR-TEM images of $\text{CuCo}_{2/1}$ NCs. i-m) EELS spectrum image of $\text{CuCo}_{2/1}$, and Co L-, O K-, C K-, and Cu L-edge elemental maps, respectively. n) elemental profile along different NCs as shown by the arrow in cobalt carbide.

components with binding energies at 288.7, 287.3, 285.7, 284.8, and 283.6 eV, corresponding to $\text{O}-\text{C}=\text{O}$, $\text{C}=\text{O}$, $\text{C}-\text{OH}$, $\text{C}-\text{C}$, and metal carbide, respectively (Figure 4a). The carbide signal was later correlated to cobalt carbide by analyzing the cobalt 2p high-resolution energy spectrum. The cobalt spectrum was deconvoluted in up to twelve peaks (excluding an LMM Auger peak at 777.0 eV, Figure 4c), with the peaks at 779.2 and 795.3 eV corresponding to the $2p_{3/2}$ and $2p_{1/2}$ orbitals of cobalt carbide, respectively. The presence of four satellite peaks at 784.3, 788.4, 801.1, and 803.2 eV associated with the cobalt carbide and Co^{2+} peaks, confirmed the presence of the carbide phase.^[49] Additional peaks were fitted to metallic cobalt (778.0, 794.1 eV), CoO (780.5, 796.5 eV), and $\text{Co}(\text{OH})_2$ (781.9, 797.8 eV). Similarly, the Cu2p XPS spectrum (Figure 4d) revealed twelve peaks, including those for Cu₂O (931.2 and 950.8 eV), metallic copper (932.6 and 952.3 eV), CuO (934.2 and 953.9 eV), and $\text{Cu}(\text{OH})_2$ (935.4 and 955.8 eV), along with satellite peaks associated with CuO (945.0, 943.3, 961.2 and 963.0 eV). The deconvolution of the O 1s spectra (Figure 4b) corroborated the presence of copper and cobalt oxides and hydroxides (CuO – 528.1 eV; CoO – 529.4 eV; Cu_2O – 530.2 eV; $\text{Cu}(\text{OH})_2$ – 531.3 eV; $\text{Co}(\text{OH})_2$ – 532.0 eV), along with $\text{C}=\text{O}$ and $\text{C}-\text{O}$ peaks (532.7 and 533.3 eV, respectively). The confirmation by XPS of a carbide phase was unexpected due to the preliminary XRD data and the synthesis conditions. Nonetheless, it has been reported the direct synthesis of Co_2C and Co_3C nanoparticles by the polyol processes as well as the presence of cobalt carbide in the synthesis of metallic cobalt nanoparticles.^[50]

In order to study the morphology and distribution of the different phases observed by XPS, HR-TEM and EELS analyses were conducted (Figure 4e–n). TEM images clearly reveal a core-shell structure, with a core ≈ 50 to 100 nm in diameter surrounded by a 5 to 10 nm thick shell. The measured d-spacing at the core (0.206 nm) matched with the [111] direction of a metallic CuCo structure, while the d-spacing at the shell (0.269 nm) agreed with the [111] direction of a CoO structure (Figure 4g). This con-

firmed the presence of a metallic core surrounded by a metal oxide shell. As previously mentioned, the core-shell domains are supported on a thin and heterogeneous nanosheet. The analysis of the area corresponding to the nanosheet revealed the presence of crystallographic planes compatible with Cu_2O (0.212 nm, [200]), CoO (0.214 nm, [200]), and Co_2C (0.221 nm, [020]) structures. This confirms the coexistence of multiple crystallographic phases within the NCs, suggesting the presence of different heterojunctions (likely a Mott-Schottky junction) that may serve as catalytic active sites, thereby enhancing the catalytic activity.^[51]

The distribution of copper and cobalt was further studied by acquiring EELS and EDX spectrum images of the NCs (Figure 4i–n; Figure S8, Supporting Information). The EELS elemental maps shown in Figure 4i–n reveal that Cu-rich areas are surrounded by Co, C, and O regions. EELS analyses performed in different regions of the self-supported NCs corroborated the concentration of copper at the cores along with traces of cobalt and oxygen in the shell (see Figure S9, Supporting Information). Noteworthy, the blunt Cu L-edge peak indicates the presence of metallic copper at the core of the NCs,^[52] whereas the shell (blue square in Figure S9, Supporting Information) shows a decrease in the copper signal and a significant increase of the Co, C, and O signals. In particular, the presence of the O signal and the sharpness of the Co L-edge indicate the presence of cobalt oxide species.

In summary, $\text{CuCo}_{2/1}$ NCs exhibit a core-shell structure with a Cu-rich metallic core coated by a shell composed of a mixture of copper and cobalt oxides, along with a Co_2C phase. It is important to note that the presence of small amounts of cobalt within the core cannot be entirely ruled out. As for the support, CoO and Co_2C phases extend outward to form the core-shell structure, forming a nanosheet that serves as support. Although CoO and Co_2C were the predominant phases identified through various characterization techniques, a minor presence of copper was detected by EELS mapping. This unique structure comprises the presence of metal-semiconductor and semiconductor-

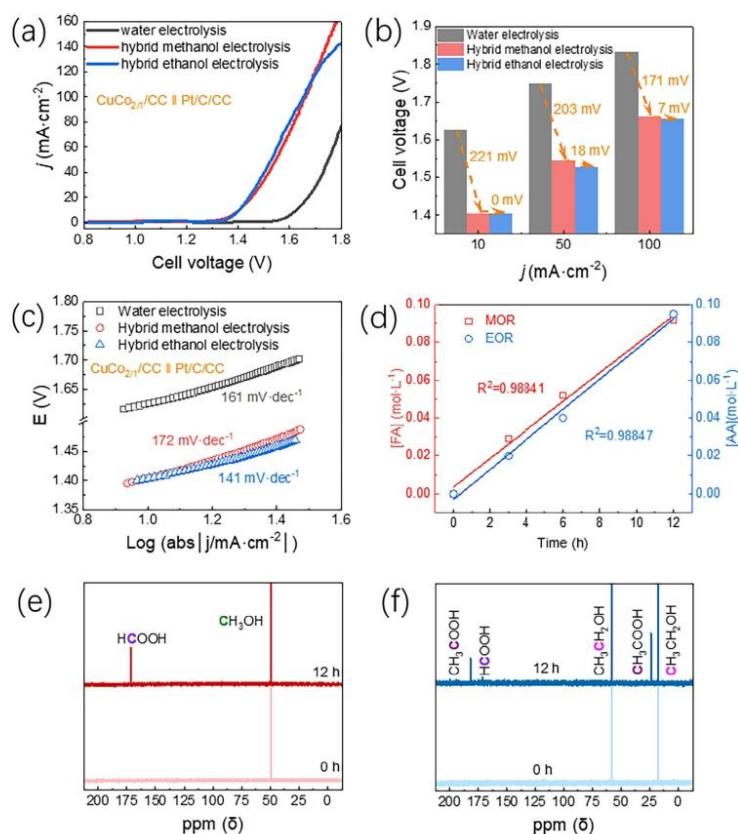


Figure 5. a) LSV polarization curves of conventional water electrolysis (1 M KOH), alcohol-assisted water splitting (1 M KOH + 1 M and 1 M KOH + 1 M ethanol) for $\text{CuCo}_{2/1}/\text{CC} \parallel \text{Pt}/\text{C}/\text{CC}$ system. b) required cell voltage comparison between conventional and alcohol-assisted water electrolysis at 10, 50, and 100 $\text{mA}\cdot\text{cm}^{-2}$, respectively. c) Tafel slopes, d) quantification of fitting curves for formate (FA) / acetate (AA) products during the methanol or ethanol assisted water electrolysis. e) ^{13}C NMR analysis of products for methanol assisted water electrolysis for 12 h under 40 $\text{mA}\cdot\text{cm}^{-2}$. f) ^{13}C NMR analysis of products for ethanol assisted water electrolysis for 12 h under 40 $\text{mA}\cdot\text{cm}^{-2}$.

semiconductor heterojunctions, which eventually may lead to an enhancement of the catalytic activity of the core due to the accumulation of charge at the interface.^[35] Indeed, catalysts comprising a heterojunction have been successfully employed for hydrogen production.^[53,54] In our particular case, the additional synergy between the core-shell domain and the nanosheet could ultimately boost the efficiency of the self-supported NCs.

2.4. Alcohol-Assisted Water Electrolysis

To demonstrate the applicability of the $\text{CuCo}_{2/1}$ catalyst for hybrid water electrolysis, a two-electrode system was set up where the anode and the cathode were functionalized with $\text{CuCo}_{2/1}$ NCs and commercial Pt/C, respectively. Both electrodes were prepared

by drop-casting the catalyst inks onto carbon cloth ($\text{CuCo}_{2/1}/\text{CC}$ and $\text{Pt}/\text{C}/\text{CC}$ electrodes). For a comparative evaluation, the $\text{CuCo}_{2/1}/\text{CC} \parallel \text{Pt}/\text{C}/\text{CC}$ system was tested in three different electrolytes (KOH, KOH + Methanol and KOH + Ethanol). First, in 1 M KOH solution (conventional water splitting, Figure 5a), the onset potential was ≈ 1.58 V. Current densities of 10, 50, and 100 $\text{mA}\cdot\text{cm}^{-2}$ were achieved under an applied potential of 1.63, 1.75, and 1.83 V, respectively, with a Tafel slope of 161 $\text{mV}\cdot\text{dec}^{-1}$. Adding methanol to the electrolyte (1 M KOH and 1 M methanol, hybrid methanol-assisted water splitting) reduced significantly the applied potentials at 10, 50, and 100 $\text{mA}\cdot\text{cm}^{-2}$ ($\Delta V = 221$, 203 and 171 mV, respectively, Figure 5b). Finally, a similar behavior was observed at lower voltages by adding ethanol (1 M KOH and 1 M ethanol, ethanol assisted water electrolysis). In particular, the onset and applied cell potential at low current density (10

$\text{mA}\cdot\text{cm}^{-2}$) are comparable to methanol-assisted water electrolysis (1.38 and 1.40 mV, respectively, Figure 5a,b). However, the applied potentials decreased at higher current density compared to methanol ($\Delta V = 18$ and 7 mV for 50 and 100 $\text{mA}\cdot\text{cm}^{-2}$, respectively). So did the Tafel slope, showing the lowest value for ethanol among all three electrolytes (141 $\text{mV}\cdot\text{dec}^{-1}$, Figure 5c). This observation aligns with the better EOR performance observed for the $\text{CuCo}_{2/1}$ NCs (Figure 3c), highlighting it as the most promising candidate for hybrid water splitting, simultaneously producing hydrogen along with value-added molecules.

To investigate the reaction products of the aforementioned process, an H-type electrolytic cell was used to separate the alcohol oxidation reaction from the hydrogen evolution reaction while preventing the reduction of products formed from the MOR and the EOR. The products were analyzed via proton and carbon NMR spectroscopy (Figure 5e,f; Figure S10, Supporting Information). In the ^{13}C NMR spectrum for the methanol-assisted water electrolysis, a peak at 171.59 ppm appeared after 12 h, indicating the presence of formate in coexistence with methanol (49.50 ppm).^[55] To evaluate the product concentration over time, ^1H NMR spectra were conducted at different time intervals (0, 3, 6, and 12 h), using maleic acid as the internal standard (6.00 ppm, shifting to 6.31 ppm Figure S10b, Supporting Information). The chemical shift observed in Figure S10 (Supporting Information) is in line with the conversion of maleic acid to fumaric acid via cis-trans isomerization.^[56] Quantitative analysis was performed by integrating the peak areas, resulting in a constant formate production over reaction time (Figure 5d). From these observations, we calculated the Faradaic efficiency for methanol-to-formate conversion, which was found to be 82.2%. This high efficiency underscores the catalyst's effectiveness in selectively producing formate as the primary reaction product.

In the context of ethanol-assisted water electrolysis, after 12 h, we observed two peaks corresponding to ethanol at 17.49 and 58.07 ppm, along with two additional peaks at 23.92 and 182.03 ppm, which can be attributed to the two different carbon environments of acetate (Figure 5f).^[57] Additionally, we observed a small peak at 171.61 ppm, indicating the presence of formate, suggesting that acetate is the primary product of ethanol oxidation, accompanied by a minor amount of formate as a byproduct. This observation is further supported by ^1H NMR results where peaks corresponding to acetate and formate are observed at 1.89 ppm and 8.63 ppm, respectively (Figure S10c,d, Supporting Information). The concentration of acetate was determined following the same procedure as in the methanol-assisted water electrolysis (blue line in Figure 5d). From this data, the selectivity for formate and acetate was 6.1% and 66.7%, respectively, resulting in a total Faradaic efficiency of 91.0% (83.3% for acetate and 7.7% for formate, respectively). Overall, the Faradaic efficiencies for MOR and EOR are comparable to the representative nanocatalysts reported in the literature, as listed in Table S4 (Supporting Information).

Based on the above discussion, we propose a rational reaction pathway for the EOR under our experimental conditions. In this mechanism, ethanol is initially oxidized to generate the key adsorbed intermediate, $^*\text{CH}_3\text{CHO}$ (Figure S11, Supporting Information). This intermediate predominantly follows a pathway leading to the formation of acetic acid as the main product. Eventually, a fraction of this acetic acid may follow further oxidation

delivering formic acid.^[58,59] This is in well, agreement with the traces of the later found in the NMR spectra. However, a small fraction of $^*\text{CH}_3\text{CHO}$ may follow alternative routes, resulting in the formation of acetaldehyde or volatile gaseous products such as CO or CO_2 . The generation of these minor byproducts may partially account for the observed decrease in FE. Further investigation, including more sensitive detection techniques such as gas chromatography or in situ spectroscopic analysis combined with DFT simulations is required to fully elucidate the reaction pathways and quantify the complete product distribution. However, this is beyond the scope of the present publication.

Finally, we studied the stability of the $\text{CuCo}_{2/1}$ catalyst by performing multistep chronopotentiometry experiments at different current densities (10, 20, 30, 40, and 50 $\text{mA}\cdot\text{cm}^{-2}$). The setup was immersed in a 1 L electrolyte solution containing 1 M KOH and 1 M methanol or ethanol to ensure an adequate alcohol supply. The current was incrementally raised every 6 h up to 50 $\text{mA}\cdot\text{cm}^{-2}$, where it was kept for 12 h before decreasing it at the same rate, leading to an overall measurement of 60 h (Figure 6a). For the methanol-assisted water electrolysis, the cell voltage increased gradually at each constant current density, with a minimal increase at low current densities (e.g., from 1.40 to 1.43 V at 10 $\text{mA}\cdot\text{cm}^{-2}$ after 6 h), and a more pronounced increase at higher current densities, reaching 1.73 V at 50 $\text{mA}\cdot\text{cm}^{-2}$ after 12 h.

This difference is clearly observed when considering the slope of the V versus t curve in Figure 6a for each current density (Table S5, Supporting Information). When decreasing the current back to 10 $\text{mA}\cdot\text{cm}^{-2}$, the voltage remained almost constant at high current densities (40 and 30 $\text{mA}\cdot\text{cm}^{-2}$) but slightly increased at low current densities. For instance, from 1.57 to 1.59 V (48 and 53 h; 30 $\text{mA}\cdot\text{cm}^{-2}$) or from 1.50 to 1.52 V (54 to 60 h; 10 $\text{mA}\cdot\text{cm}^{-2}$). Indeed, after 60 h, the final voltage did experience an increase of 0.13 V with respect to the voltage at the same current density but at time zero. The same study was conducted for ethanol-assisted water electrolysis providing a similar trend. The initial potential of 1.40 V at 10 $\text{mA}\cdot\text{cm}^{-2}$ gradually increased over time, with the applied current density reaching 1.73 V at 50 $\text{mA}\cdot\text{cm}^{-2}$ after 60 h (see Table S5, Supporting Information). Nevertheless, when decreasing the applied current density, the cell voltage remained almost constant at any step, delivering a final cell voltage of 1.44 V at 10 $\text{mA}\cdot\text{cm}^{-2}$. This represents an increase with respect to the cell voltage at time zero of 0.04 V (ca. 2.8%). This underlines the better stability of the NCs for the ethanol-assisted water electrolysis.

The voltage increase over time could be attributed to different factors, such as a rapid consumption of alcohol molecules in solution (methanol or ethanol) during the reaction or the transformation of the NCs. By comparing the LSV curves of the NCs before and after the multistep chronopotentiometry in methanol and ethanol, we observed a significant shift of the curve at higher voltages for the MOR, while for EOR, the curves were maintained (Figure S12a,d, Supporting Information). In order to elucidate the influence of alcohol consumption against catalyst transformation, after the chronopotentiometry the electrolyte was replaced by a fresh solution and additional 6 h at 10 $\text{mA}\cdot\text{cm}^{-2}$ was carried out (Figure S12b,e, Supporting Information). Interestingly, the initial potential for methanol was higher than the initial potential at the start of the multistep chronopotentiometry (1.53 V against 1.40 V) after electrolyte replacement. Conversely,

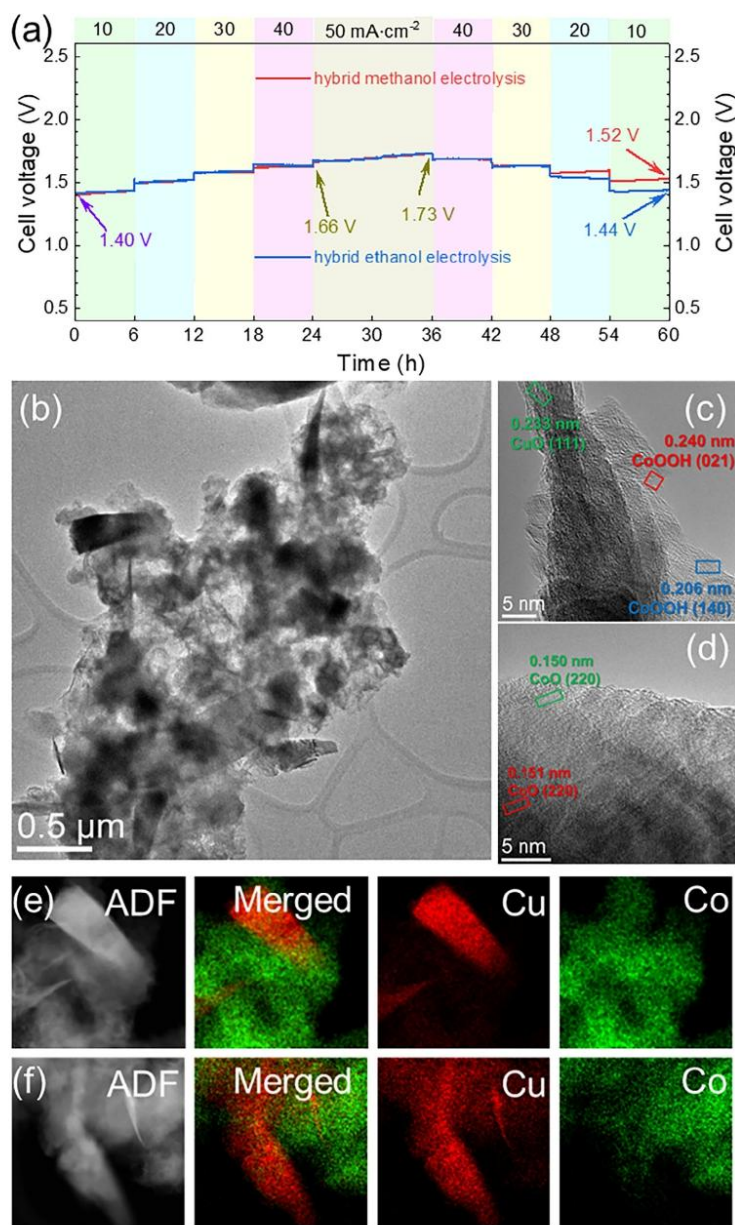


Figure 6. a) Chronopotentiometry of $\text{CuCo}_{2/1}/\text{CC} \parallel \text{Pt}/\text{C}/\text{CC}$ system in 1 M KOH + 1 M methanol (red line) and 1 M KOH + 1 M ethanol (blue line). b) TEM image of the $\text{CuCo}_{2/1}$ samples after 60 h chronopotentiometry for ethanol-assisted water ethanol electrolysis. c,d) HR-TEM images focusing on NCs and NPs in Figure 6b, respectively. e,f) EDX mapping of the $\text{CuCo}_{2/1}$ sample after chronopotentiometry test.

for ethanol, the potential remained consistent (1.41 V). After 6 h at constant current densities, the cell potential increases (1.56 and 1.44 V for methanol and ethanol, respectively). From this observation, we conclude that methanol-assisted water electrolysis did have a strong inference in the catalyst structure, while for ethanol, the addition of fresh electrolyte seems to restore the performance completely. This trend was supported by EIS analysis, where the R_{ct} for methanol increased from 0.75 Ω up to 3.85 Ω after the chronopotentiometry. Remarkably, after replacing the electrolyte, the R_{ct} further increased to 8.49 Ω . The same trend was observed for the mass transfer resistance (R_{mt}) of MOR. As for the EOR, the increases in both resistances were moderate but clearly far below those increases observed for MOR. In particular, the R_{mt} values increased within the same order of magnitude (104 to 351 Ω). Noteworthy, by replacing the old electrolyte with a fresh one, the resistances for both alcohol oxidation reactions increased. This clearly indicates that the increases measured for the cell voltages during the chronopotentiometry tests are rather related to the evolution of the catalyst's structure.

A deeper understanding of the structural evolution of the core-shell self-supported nanostructures was obtained by analyzing $\text{CuCo}_{2/1}$ NCs after the chronopotentiometry. As shown in Figure 6, NCs underwent a significant morphological transformation after the long-term stability test in ethanol, resulting in the formation of self-supported large and elongated nanostructures. These elongated domains show d-lattice spacings corresponding to the [111] plane of CuO, which confirmed the oxidation of the pristine copper core. The shell of the NCs also evolved, resulting in the formation of CoOOH ([021] and [140] planes) and CoO ([220] plane) phases. EDX and EELS elemental mapping of the $\text{CuCo}_{2/1}$ NCs confirmed the redistribution of elements along the NCs (Figure 6e,f; Figure S12, Supporting Information). Noteworthy, we observed that areas containing both cobalt (778 and 792 eV) and copper (929 and 950 eV) oxides were surrounded by areas in which only one of the oxides was present. The energies and shape of the spectra were in agreement with the oxidation state of cobalt and copper, confirming that the core underwent an oxidation process. This particular configuration would corroborate the outstanding performance of the NCs as CuO domains are surrounded by CoO and CoOOH ones. In particular, the latter have been identified as a true active species for OER, likely acting as active sites boosting the electrocatalytic activity of CuO.^[60] XPS analysis of the NCs after the EOR stability test further supports our findings (Figure S13, Supporting Information). A detailed deconvolution of the Co 2p energy region was performed to resolve overlapping components assigned to CoO (780.5 eV, 795.5 eV) and CoOOH (782.3 eV, 797.1 eV). Compared to the spectra of the as-synthesized NCs, the metallic cobalt signals are no longer observed, indicating their transformation. Furthermore, part of the Co^{2+} species is oxidized to CoOOH. Similarly, deconvolution of the Cu 2p region reveals peaks corresponding to metallic Cu (932.7 eV, 952.1 eV), CuO (934.8 eV, 954.3 eV), and CuOOH (936.3 eV, 956.4 eV). While the metallic Cu signal remains detectable, it is significantly diminished, and the emergence of CuOOH indicates partial oxidation of Cu^{2+} to higher-valence states. These findings are consistent with the EELS characterization discussed above, confirming a structural evolution in which Co and Cu atoms diffuse from the metallic core toward the formation of heterojunctions. A similar structure evolution

was observed for NCs after chronopotentiometry in the presence of methanol (Figures S14 and S15, Supporting Information).

3. Conclusion

We successfully developed a complex yet ordered bimetallic Cu/Co Mott-Schottky nanohybrid structure using a simple and rapid one-pot microwave-assisted method. This structure features a metallic Cu/Co core, surrounded by a mixture of copper oxide, cobalt oxide, and cobalt carbide phases extending into nanosheets providing support for the Cu/Co core. The NCs evolve from the original Mott-Schottky heterostructure into a CuO-CoOOH-CoO composite during electrolysis.

The resulting architecture features a rich array of heterogeneous interfaces, significantly enhancing the oxidation activity toward methanol and ethanol. The observed increase in activity can be attributed to the induced and enhanced self-driven charge transfer within the heterogeneous structure, which balances the adsorption of reactants and the desorption of products. When employing these NCs as anode for alcohol-assisted water electrolysis, potentials are clearly reduced compared to conventional water electrolysis while maintaining stability for over 60 h. Moreover, alongside the hydrogen evolution reaction, formic and acetic acids are produced at the anode, achieving high selectivity and Faradaic efficiency (91.0% for ethanol oxidation). These findings provide a novel experimental approach for synthesizing multi-interface, high-activity heterogeneous structures, offering additional strategies to address the high cell potential required for conventional water electrolysis and enhancing the overall value of the reaction process.

4. Experimental Section

Materials: Cobalt(II) acetylacetonate ($\text{Co}(\text{acac})_2$, $\geq 99.9\%$), copper(II) acetylacetonate ($\text{Cu}(\text{acac})_2$, $\geq 99.9\%$), benzyl alcohol (for synthesis), potassium hydroxide (KOH, 85% ACS reagent), nafion 117 containing solution ($\approx 5\%$ in a mixture of low aliphatic) and 2-propanol ($\geq 99.5\%$) were purchased from Sigma-Aldrich. Polyvinylpyrrolidone (PVP_{3.5k}, Mw = 3'500) was purchased from Thermo Fisher Scientific. Carbon black (Vulcan CX-72) was purchased from FuelCellStore. All materials were used as received without further purification. Milli-Q water (18.2 M Ω -cm, Milli-Q IQ, Merck Millipore) was used for all the experiments and solutions. Commercial Pt/C catalyst (20wt% of Pt loading) was purchased from QuinTech. Carbon cloth (W051101) was purchased from CeTech Co., Ltd.

MW-Assisted Synthesis of Cu/Co NCs: For the MW-assisted synthesis of Cu/Co NCs, a MW reactor (CEM Discover SP) operating at a frequency of 2.45 GHz and a power of 300 W was used. Samples were produced by modifying a procedure for the synthesis of Cu_2O NCs previously reported by the group.^[42] The amount of benzyl alcohol and PVP_{3.5k} were kept constant to 4 mL and 136 mg (0.038 mmol), respectively. The copper to cobalt molar feeding ratio was modified keeping a final metal concentration of 17.5 mM (Co + Cu). For instance, for a 2:1 copper to cobalt ratio, 136 mg of PVP_{3.5k} (0.038 mmol) were dissolved in 4 mL of benzyl alcohol through continuous sonication (20 min) in a 10 mL reaction tube. Next, 12.30 mg of $\text{Cu}(\text{acac})_2$ (0.047 mmol) and 5.90 mg of $\text{Co}(\text{acac})_2$ (0.023 mmol) were added into the reaction tube, and the solution was sonicated further until a homogeneous solution was formed (ca. 30 min). The final solution was then purged by bubbling with an Ar flow for at least 20 min and the tube was sealed with a rubber. Finally, the tube was placed inside the MW reactor, heated to 60 °C, and kept at that temperature for 5 min. The temperature was then raised up to 200 °C (ca. 180 seconds) and kept at 200

°C for 10 min before cooling down to room temperature with compressed air. The NCs were collected by adding 30 mL of acetone followed by centrifugation at 6000 rpm for 10 min. The supernatant was discarded and the procedure repeated at least 3 times before drying the precipitate under vacuum at room temperature. Based on the copper-to-cobalt molar ratio, the sample was labelled as CuCo_{2/1}.

Samples with different copper to cobalt molar ratios were synthesized following the same procedure but adjusting the feeding Cu(acac)₂ and Co(acac)₂ ratios. In detail, the copper: cobalt feeding molar ratio was adjusted to 1:4, 1:2, 1:1 and 4:1 leading to the synthesis of the CuCo_{1/4}, CuCo_{1/2}, CuCo_{1/1}, CuCo_{2/1}, CuCo_{4/1} samples, respectively. Additionally, control samples using only Cu(acac)₂ or Co(acac)₂ (1:0 or 0:1 molar ratio) were synthesized. These samples were labeled as Cu₂O (CuCo_{1/0}) and CoO (CuCo_{0/1}), respectively.

NCs Characterization—X-Ray Characterization—X-Ray Diffraction (XRD): Patterns were collected using a conventional Cu-K α radiation source ($\lambda = 1.5406$ Å) in a Bruker ADVANCE D8 employing a Bragg-Brentano geometry. Intensity was recorded within the 2θ range from 20° to 80° at a scanning step of 0.02° s⁻¹. Samples were prepared by drop-casting and further evaporating a concentrated solution of NCs onto an amorphous silicon wafer.

NCs Characterization—Electron Transmission Microscopy (TEM) and High-Resolution TEM (HR-TEM) Analysis: Low-resolution electron micrographs were obtained using a JEOL 1210 TEM operating at 120 kV, equipped with a side-entry 60°/30° double tilt GATAN 646 specimen holder. High-resolution TEM (HR-TEM) images, high-angle annular dark-field scanning TEM (HAADF-STEM) images, and electron energy loss spectroscopy (EELS) mapping were conducted by a Spectra 300 (S)TEM operated at 300 kV (Thermo Fisher). Samples were prepared by drop-casting a diluted solution of NCs onto carbon-coated Au-grids or Cu-grids (400 mesh).

NCs Characterization—X-Ray Photoelectron Spectroscopy (XPS): XPS measurements were done in a SPECS PHOIBOS 150 hemispherical energy analyzer using Al K α X-ray radiation (1486.6 eV) for excitation.

NCs Characterization—Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-OES): To determine the final copper to cobalt ratio in the NCs, as well as the yield of the reaction, ICP-OES was carried out using an Agilent model 5900. Samples were prepared by digesting ≈ 1 mg of NCs in 1 mL of aqua regia for 30 min. The solution was diluted with Milli-Q water reaching a final volume of 10 mL.

Electrochemical Characterizations: The electrochemical performance of each sample was analyzed utilizing a Bio-logic VSP multichannel potentiostat. A conventional three-electrode cell configuration was employed where a 5 mm diameter glassy carbon disk was used as the working electrode (WE), a platinum mesh as the counter electrode (CE) and a Hg/HgO electrode as the reference electrode (RE). Cyclic voltammetry (CV) in 1 M KOH at a sweeping rate of 50 mV s⁻¹ was performed for each catalyst.

Electrochemical Characterizations—Preparation of the catalyst: The NCs produced were supported onto carbon black to prepare the catalyst and evaluate their electrocatalytic activity. In detail, 4 mg of Cu/Co NCs and 2 mg of carbon black (2:1, mass ratio) were dispersed in 5 mL of ethanol through continuous sonication for 3 h to ensure a homogenous mixing. The suspension was then dried under vacuum at 60 °C for 12 h. Finally, 5 mg of the dried catalyst was dispersed in a 1 mL of solution (200 μ L of Milli-Q water, 700 μ L of 2-propanol and 100 μ L of Nafion) and sonicated for 30 min until a homogenous ink was formed.

Electrochemical Characterizations—Preparation of the WE: First, the surface of the electrode was polished with alumina powder until achieving a mirror-like surface. Afterwards, 5 μ L of the catalyst ink containing the Cu/Co NCs was drop-casted onto the WE surface. All potentials were corrected to the reversible hydrogen electrode (RHE) according to the following equation: $E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.059 \cdot \text{pH} + 0.098$ V, where the pH was determined by a pH meter.

Electrochemical Characterizations—OER, MOR and EOR Characterization: For evaluating the performance of the samples for OER, MOR and EOR, CV curves were acquired in a KOH solution containing different concentrations of methanol or ethanol (0, 0.5, 1, 2, and 4 M). Tafel slopes were determined from Tafel plots following the equation: $\eta = b \cdot \log j + c$,

where b is the Tafel slope, η is the overpotential and j is the current density. Electrochemical double-layer capacitance (C_{dl}) curves were measured by running CV curves in the non-Faradaic region (1.174–1.274 V vs RHE) at different scan rates (from 20 to 100 mV s⁻¹). The C_{dl} was calculated by following the equation: $C_{\text{dl}} = \Delta j/v$, where $\Delta j = (j_{\text{a},2} - j_{\text{c},2})/2$ is the current density (at 1.224 V vs RHE, mA cm⁻²) and v is the scan rate (mV s⁻¹). The electrochemical active surface area (ECSA) was calculated as: $\text{ECSA} = C_{\text{dl}}/C_s$, where a general specific capacitance (C_s) of 0.04 mF cm⁻² in 1 M KOH was used.^[61] Electrochemical impedance spectroscopy (EIS) was acquired with an amplitude of 5 mV at frequencies ranging from 10⁶ to 10⁻² Hz. Finally, the mass activity (MA) of the catalyst was calculated according to the following equations: $\text{MA} = j/m$, where j is the measured current density (mA cm⁻²) and m is the mass of NCs. Partial iR compensation (90%) was applied to all data manually.

Electrochemical Characterizations—Alcohol-Assisted Water Electrolysis: Conventional and hybrid water electrolysis were evaluated using a two-electrode configuration employing a HCl-activated carbon cloth (CC) (1 $\times$ 1.5 cm²) as both anode and cathode. Electrodes were prepared by drop-casting a solution containing as-prepared CuCo_{2/1} NCs (anode) or commercial Pt/C (cathode). For instance, 5 mg of CuCo_{2/1} NCs were dispersed in a solution containing 200 μ L of MQ-H₂O, 700 μ L of 2-propanol, and 100 μ L of Nafion under 3 h of sonication. Next, 200 μ L of this solution was drop casted onto the CC to achieve a loading of 1 mg cm⁻². The anode was labeled as CuCo_{2/1}/CC. The same procedure was used to prepare the cathode, but the CuCo_{2/1} NCs were replaced by commercial Pt/C. In this case, 400 μ L were drop casted onto the CC to achieve 2 mg cm⁻² (anode labeled as Pt/C/CC).

Linear sweep voltammetry (LSV) was applied to both anodes in a 1 M KOH electrolyte solution (conventional water splitting) and in a 1 M KOH electrolyte solution containing 1 M methanol and ethanol concentrations (hybrid alcohol electrolysis). Data were analyzed using the same equations described previously. Stability tests were carried out by running chronopotentiometry measurements at 10, 20, 30, 40, and 50 mA cm⁻² for 60 h for hybrid methanol- and ethanol-water splitting.

Electrochemical Characterizations—Characterizations of the Products: To characterize the byproducts of the alcohol-assisted water electrolysis, the electrolyte was analyzed after chronopotentiometry measurements at 40 mA cm⁻² over time (0, 3, 6, 12 h) in an H-type cell employing a Nafion 117 membrane. In detail, 0.3 mL of the electrolyte was mixed with 0.3 mL of D₂O and ¹³C and ¹H nuclear magnetic resonance (NMR) spectroscopies were carried out in a Bruker Avance III HD 400 MHz. For a quantitative analysis, maleic acid (0.1 mL) was used as an internal standard.^[55] The corresponding selectivity (S) and faradaic efficiencies (FE) for each reaction were calculated at a static current at different times using the following equations:

$$S(\%) = \frac{N}{N_{\text{OH}}} \cdot 100; \text{FE}(\%) = \frac{\sum N_i \cdot 4F}{Q} \cdot 100 \quad (1)$$

Where N is the moles of the as-produced molecule, N_{OH} is the moles of consumed alcohol (methanol or ethanol), Q is the total charge passed through the system recorded during electrolysis, and F is the Faraday constant (96485 C mol⁻¹).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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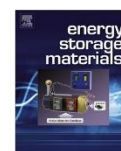
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- [40] M. Yuan, J. Chen, Y. Bai, Z. Liu, J. Zhang, T. Zhao, Q. Wang, S. Li, H. He, G. Zhang, *Angew. Chem. – Int. Ed.* **2021**, *60*, 10910.
- [41] Q. Dong, H. Wang, F. Liu, J. Ren, H. Wang, X. Wang, R. Wang, *J Mater Chem A Mater* **2023**, *11*, 4717.
- [42] M. Torras, A. Roig, *Cryst. Growth Des.* **2021**, *21*, 5027.
- [43] K. J. Carroll, J. U. Reveles, M. D. Shultz, S. N. Khanna, E. E. Carpenter, *J. Phys. Chem. C* **2011**, *115*, 2656.
- [44] X. Zhong, Y. Zhang, Z. Geng, F. Shi, M. Jiang, Y. Sun, X. Wu, K. Huang, S. Feng, *Inorg. Chem. Front.* **2019**, *6*, 1660.
- [45] J. Zhang, C. Zhang, X. Duo, Z. Liu, C. Liu, L. Guo, A. Xie, S. Luo, *Ionics* **2020**, *26*, 5123.
- [46] Y. Chen, J. Mao, H. Zhou, L. Xing, S. Qiao, J. Yuan, B. Mei, Z. Wei, S. Zhao, Y. Tang, C. Liu, *Adv. Funct. Mater.* **2024**, *34*, 2311664.
- [47] L. Chen, Z. Hua, J. Shi, M. He, *ACS Appl. Mater. Interfaces* **2018**, *10*, 39002.
- [48] Z. Wang, X. Liao, M. Zhou, F. Huang, K. A. Owusu, J. Li, Z. Lin, Q. Sun, X. Hong, C. Sun, Y. Cheng, Y. Zhao, L. Mai, *Energy and Environmental Materials* **2023**, *6*, 12409.
- [49] Y. Wu, Z. Xiao, Z. Jin, X. Li, Y. Chen, *J. Colloid Interface Sci.* **2021**, *590*, 321.
- [50] W. Yang, S. Rehman, X. Chu, Y. Hou, S. Gao, *ChemNanoMat* **2015**, *1*, 376.
- [51] S. Pal, T. Ahmed, S. Khatun, P. Roy, *ACS Appl. Energy Mater.* **2023**, *6*, 7737.
- [52] D. H. Pearson, C. C. Ahn, B. Fultz, *Phys. Rev. B* **1993**, *47*, 8471.
- [53] J. Hou, Y. Sun, Y. Wu, S. Cao, L. Sun, *Adv. Funct. Mater.* **2018**, *28*, 1704447.
- [54] M. Wu, J. Zhao, C. Li, R. Liu, *J Mater Chem A Mater* **2022**, *10*, 4791.
- [55] J. Shao, Y. Fang, X. Wu, M. I. Abdullah, Y. Tao, *Nano Res.* **2024**, *17*, 2388.
- [56] W. Chen, X. Chen, S. Yi, *ACS Omega* **2019**, *4*, 8274.
- [57] H. Sun, L. Li, Y. Chen, H. Kim, X. Xu, D. Guan, Z. Hu, L. Zhang, Z. Shao, W. C. Jung, *Appl. Catal. B* **2023**, *325*.
- [58] T. H. Tan, J. Scott, Y. H. Ng, R. A. Taylor, K. F. Aguey-Zinsou, R. Amal, *ACS Catal.* **2016**, *6*, 8021.
- [59] D. S. Muggli, J. T. McCue, J. L. Falconer, *J. Catal.* **1998**, *173*, 470.
- [60] X. Ren, Y. Dai, X. Wen, B. Guo, C. Shi, X. Huang, Y. Guo, S. Li, *Adv Sustain Syst* **2024**, *8*, 2300379.
- [61] C. C. L. McCrory, S. Jung, J. C. Peters, T. F. Jaramillo, *J. Am. Chem. Soc.* **2013**, *135*, 16977.



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Enhanced lithium polysulfide adsorption and reaction with cobalt-doped spinel additives for robust lithium-sulfur batteries

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ABSTRACT

Sulfur-based cathodes offer a promising high-energy-density alternative to conventional lithium-ion batteries. However, their commercial viability is hindered by limited stability due to the gradual loss of active sulfur during cycling. This study addresses this challenge by introducing a cobalt-doped spinel oxide as a catalytic additive, designed to enhance the performance and stability of sulfur cathodes with minimized cobalt usage. Small amounts of cobalt doping improve the adsorption of sulfur species through stronger electronic interactions with antibonding orbitals and accelerate charge transfer, thereby promoting more efficient sulfur redox reactions. Cobalt also lowers the energy barrier for Li_2S formation, a critical step in the cycling process. Specifically, Co-doped MnFe_2O_4 with 2.4 wt % Co demonstrates a remarkable initial capacity of 1302 mAh/g at 0.1C, excellent rate capability with 700 mAh/g at 4C, and stable cycling performance with an average capacity decay of just 0.03 % per cycle at 0.5C over 200 cycles. Overall, this work underscores the potential of cobalt-doped spinel structures as catalytic additives to mitigate the limitations of sulfur cathodes, paving the way for more stable and high-performance lithium-sulfur batteries.

1. Introduction

Since the early 21st century's surge in smart technology-driven mobility, the demand for lithium-ion batteries (LIBs) has skyrocketed, rising more than twentyfold from approximately 30 GWh in 2011 to over 750 GWh in 2023, predominantly propelled by the electric vehicle (EV) sector [1]. The forecast for LIB demand by 2030 exceeds 3 TWh [2]. Although LIBs have significantly evolved in performance since their inception, they are nearing their practical energy density limits, which

remain below the optimal requirements for the EV market [3–7]. Additionally, despite the substantial reduction in LIB cell costs, the limited availability of lithium and other critical elements heavily utilized in current cathode designs like cobalt, could potentially reverse this cost-reduction trend [8,9].

In this context, lithium-sulfur batteries (LSBs) with a remarkable theoretical energy density of 2600 Wh/kg, far surpassing that of LIBs, emerge as a highly promising alternative for next-generation energy storage [10–13]. The projected lower costs of LSBs, driven by the

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abundant availability of sulfur, position them as an attractive option for EVs, portable devices, and even stationary energy storage systems [14–16]. Despite these advantages, the commercialization of LSBs is hindered by several significant challenges. One of the primary issues is the dissolution of lithium polysulfides (LiPS) in commonly used ether-based electrolytes, which leads to poor coulombic efficiency and shortens battery lifespan [17–22]. Furthermore, the inherently sluggish reaction kinetics of the Li-S redox process and the incomplete utilization of sulfur result in reduced charge/discharge rates and lower effective capacity. To address these limitations, the development of cathode additives able to trap LiPS and accelerate their conversion is critical. By doing so, these additives have the potential to significantly enhance the electrochemical performance of LSBs, improve sulfur utilization, and extend the battery's lifespan, paving the way for more efficient and durable energy storage solutions [23–25].

Transition metals effectively interact with LiPSs by forming metal-sulfur bonds, which both trap LiPSs and weaken their S-S bonds thus facilitating their breaking [26]. This dual action not only mitigates the shuttle effect but also speeds up the sulfur reduction reaction, enhancing LSB performance [27,28]. Integrating these metals in the form of metal oxide nanoparticles, allows both stabilizing them under relevant working conditions while maximizing catalytic site exposure [29]. In this context, spinel-type transition metal oxide (AB_2O_4) nanoparticles are of particular interest as cathode additives in LSBs [29–32]. They offer polar surfaces that promote efficient LiPS adsorption and improve the Li-S reaction kinetics [33–36]. In these structures, oxygen ions create a cubic close-packed lattice, with divalent cations (A) in tetrahedral sites and trivalent cations (B) in octahedral sites.

Our previous research, along with other studies, has demonstrated that incorporating spinel catalysts into LSB cathodes significantly enhances the phase transition of LiPSs, thereby boosting conversion efficiencies [29,30,37]. However, the inherent poor conductivity of spinel oxides remains a notable limitation that can adversely affect LSB performance [34,38]. Additionally, the effectiveness of these catalysts is highly dependent on their chemical composition, which can be strategically tailored to optimize their chemical affinity for LiPSs.

In terms of composition, cobalt-containing materials stand out as particularly promising candidates due to their strong Co-S bonding energies, which improve charge transfer rates and effectively mitigate the polysulfide shuttle effect [26,27,29,30,39–44]. Despite these advantages, the cost, environmental concerns, and ethical issues associated with cobalt extraction underscore the urgency of developing strategies to minimize cobalt usage in current and future energy storage technologies, including LSBs [45].

Efforts to optimize and minimize cobalt usage in activating the Li-S reaction within LSB cathodes have focused on dispersing cobalt as single atoms on the surface of carbon supports or as a dopant within metal oxides, chalcogenides, phosphides and other metal compounds [41,43,46–49]. While both approaches effectively limit cobalt consumption, the latter is particularly advantageous due to its simplicity and cost-efficiency, making it more suitable for large-scale industrial applications. Despite these advancements, the precise effects of controlled cobalt doping on the performance of spinel oxides in LSBs remain underexplored, presenting a significant opportunity for further research and development, aimed at designing and engineering advanced and cost-effective catalytic additives for sulfur cathodes.

This study investigates the influence of varying cobalt doping levels in spinel oxides on the electrochemical performance of LSBs. Utilizing Co-doped MnFe_2O_4 nanoparticles synthesized through a hydrothermal method, we explore a range of cobalt concentrations. Our findings indicate that minimizing cobalt usage, reducing it to 2.4 %, enhances battery performance compared to samples with higher cobalt content. This improvement is attributed to the increased adsorption energies of LiPS and Li_2S_8 on isolated cobalt atoms within the spinel structure, which are crucial for boosting the electrocatalytic efficiency of LSBs. Comprehensive electrochemical, morphological, and compositional

analyses, alongside density functional theory (DFT) calculations, are used to support these findings and suggest that optimizing cobalt levels in spinel-based materials can lead to more efficient and durable LSBs.

2. Results and discussion

MnFe_2O_4 and Co-doped MnFe_2O_4 with nominal Co weight ratios of 0.5 % ($\text{Co}_{0.02}\text{-MnFe}_2\text{O}_4$), 2.4 % ($\text{Co}_{0.1}\text{-MnFe}_2\text{O}_4$), and 4.8 % ($\text{Co}_{0.2}\text{-MnFe}_2\text{O}_4$), were synthesized using a hydrothermal method (Fig. 1a). Scanning electron microscopy (SEM) images reveal the materials to consist of aggregated particles with an average size of ca. 80 nm (Figure S1). Energy dispersive X-ray spectroscopy (EDS) and inductively coupled plasma-optical emission spectroscopy (ICP-OES) analyses show the Co concentration to be consistent with the nominal amount of Co introduced (Table S1). Transition electron microscopy (TEM) and high-resolution TEM (HRTEM) analyses show the particles to present irregular morphologies but have faceted surfaces (Figs. 2b, and S1). Power spectrum fast Fourier transformation (FFT) analysis reveals a cubic atomic arrangement with space group 227 (Fig. 2b). Additionally, high-angle annular dark field (HAADF) and scanning TEM-EDS (STEM-EDS) composition maps of Co- MnFe_2O_4 show a homogeneous distribution of the different elements with no segregated phase (Fig. 2c).

Powder X-ray diffraction (XRD) patterns of all the samples match the cubic MnFe_2O_4 spinel structure $Fd\bar{3}m$ (JCPDS: 010–0319, Fig. 1d). With the increasing amount of Co, a shift to higher 2 θ diffraction angles is observed (Fig. 1e) pointing towards a lattice shrinkage. This result is further corroborated by HRTEM analysis (Fig. 1b, blue square, and Figure S2), which reveals a contraction in the interplanar spacing of the $\text{Co}_{0.2}\text{-MnFe}_2\text{O}_4$ sample at the (111) plane compared to MnFe_2O_4 . The lattice narrowing can be attributed to the partial substitution of Fe^{3+} ions with Co^{2+} , as Co^{2+} has a smaller ionic radius (0.58 Å) than Fe^{3+} (0.67 Å) [50].

The high-resolution X-ray photoelectron spectroscopy (XPS) analysis of MnFe_2O_4 and Co-doped MnFe_2O_4 reveals distinct changes in the oxidation states of manganese and iron due to cobalt doping (Fig. 1f). Upon Co addition, the Mn 2p XPS spectrum shows a redshift, indicating the partial oxidation of Mn^{2+} to Mn^{3+} . Conversely, the Fe 2p XPS spectra of the Co-doped MnFe_2O_4 sample are blue-shifted, suggesting the partial reduction of Fe^{3+} to Fe^{2+} .

The polysulfide-anchoring capacities of MnFe_2O_4 and Co- MnFe_2O_4 were experimentally evaluated by suspending equal amounts of each material in a 5 mmol L^{-1} Li_2S_4 solution in 1,3-dioxalane (DOL) and 1,2-dimethoxyethane (DME) in a volume ratio 1:1 and observing changes in the characteristic yellow color of the Li_2S_4 solution (Fig. 2a). After 6 h of LiPS adsorption, the solution was lighter for all materials, indicating some extent of LiPS adsorption. The vial containing $\text{Co}_{0.1}\text{-MnFe}_2\text{O}_4$ displayed the palest color, suggesting superior LiPS adsorption capabilities. This observation was further supported by UV–Vis spectroscopy, where $\text{Co}_{0.1}\text{-MnFe}_2\text{O}_4$ exhibited the lowest absorbance intensity below 350 nm, indicating strong Li_2S_4 adsorption, further confirming its enhanced polysulfide anchoring capability (Figure S3a). Additionally, the Mn 2p and Fe 2p XPS spectra of both MnFe_2O_4 and $\text{Co}_{0.1}\text{-MnFe}_2\text{O}_4$ were red-shifted after exposure to LiPS, indicating a chemical interaction (Figure S3b and 2b). Notably, the shift in $\text{Co}_{0.1}\text{-MnFe}_2\text{O}_4$ was more pronounced, evidencing a stronger interaction with LiPS. These experimental results suggest that cobalt doping in MnFe_2O_4 significantly enhances its interaction with LiPS, reducing their solubility and increasing surface coverage, which is reflected in the chemical environment of the surface metal atoms in the oxide spinel. The Brunauer-Emmett-Teller (BET) specific surface area of $\text{Co}_{0.1}\text{-MnFe}_2\text{O}_4$ was 20.5 $\text{m}^2 \text{g}^{-1}$ (Figure S4).

Since the LiPS adsorption takes place on the catalyst's surface, a lattice model incorporating Co-doped MnFe_2O_4 at the materials surface was adopted. Accordingly, the adsorption configuration of three different sulfur-containing species (Li_2S_4 , Li_2S_2 , and Li_2S) on MnFe_2O_4 and $\text{Co}_{0.1}\text{-MnFe}_2\text{O}_4$ surfaces were optimized using DFT calculations, as

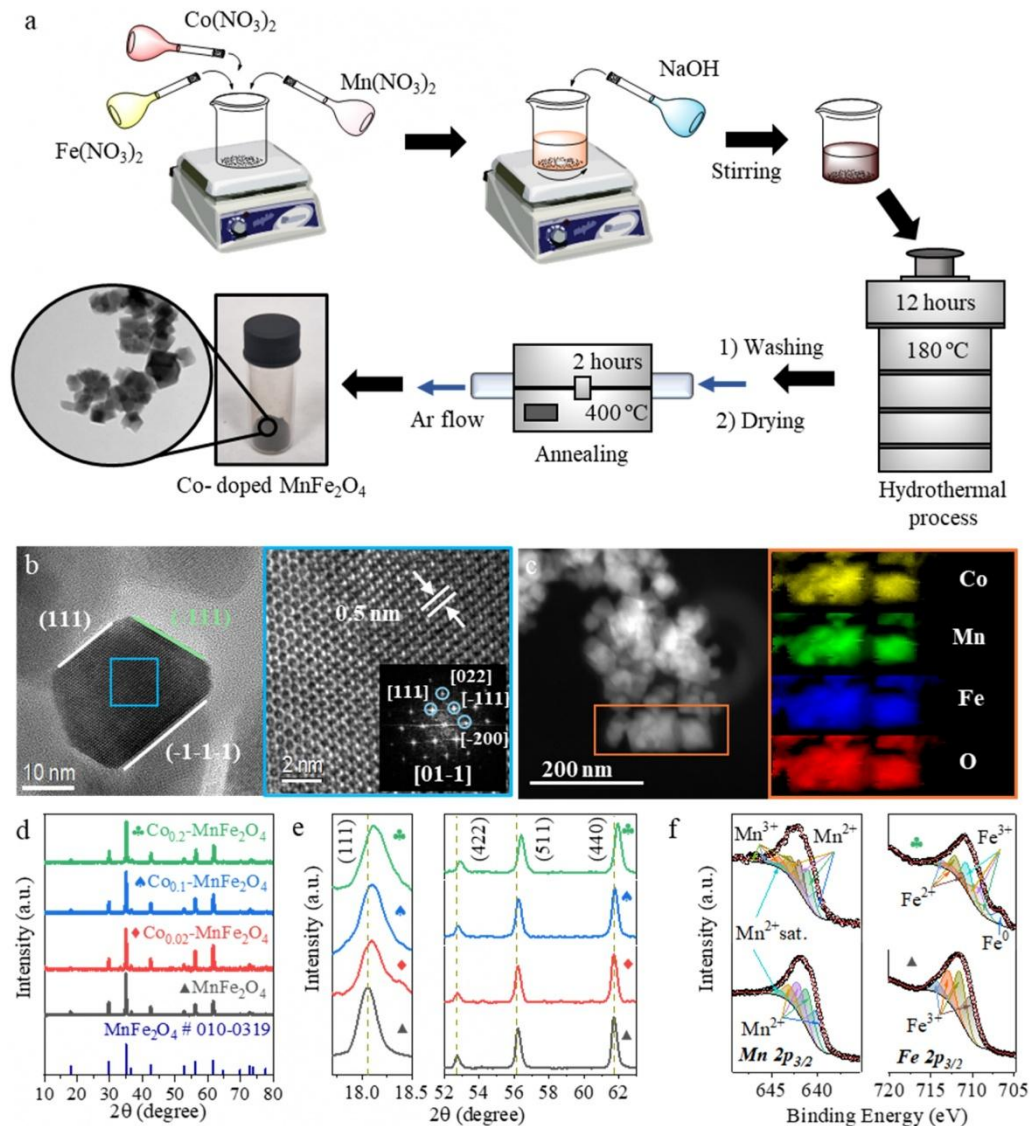


Fig. 1. (a) Scheme of the experimental procedure used to prepare Co-doped MnFe₂O₄ by hydrothermal method. Characterization of MnFe₂O₄, Co_{0.2}-MnFe₂O₄, Co_{0.1}-MnFe₂O₄, and Co_{0.02}-MnFe₂O₄ and (b) HRTEM micrographs of the Co_{0.2}-MnFe₂O₄ sample. The lattice fringes visualized in the blue square magnified detail correspond to the (111), (022), (-111), and (-200) crystal planes of MnFe₂O₄ along its [01-1] zone axis. (c) HAADF-STEM image and STEM-EDS composition maps of Co_{0.2}-MnFe₂O₄. The L-edge of Co at 779 eV (yellow), Mn at 640 eV (green), and Fe at 708 eV (blue), along with the K-edge of O at 532 eV (red), were used in the analysis. (d,e) XRD patterns. (f) Mn 2p_{3/2} and Fe 2p_{3/2} XPS spectra of MnFe₂O₄ (down) and Co_{0.2}-MnFe₂O₄ (up).

shown in Figs. 2c and S5–8. Co_{0.1}-MnFe₂O₄ exhibited more negative adsorption energy values compared to MnFe₂O₄, indicating that Co-doping enhances the binding strength between the sulfur species and the sample surface. Notably, the adsorption energy of Li₂S increased by 34 % for Co_{0.1}-MnFe₂O₄ relative to MnFe₂O₄.

DFT calculations were also used to analyze the Gibbs free energy

changes along the S reduction pathway at the MnFe₂O₄ and Co_{0.1}-MnFe₂O₄ surfaces (Fig. 2d). Consistently with previous reports, the solid-state transformation from Li₂S₂ to Li₂S was found to be the rate-limiting step of the sulfur reduction process, thus significantly influencing the lithiation kinetics [50]. The results indicate that the Gibbs free energy for this step at the Co_{0.1}-MnFe₂O₄ surface is notably lower

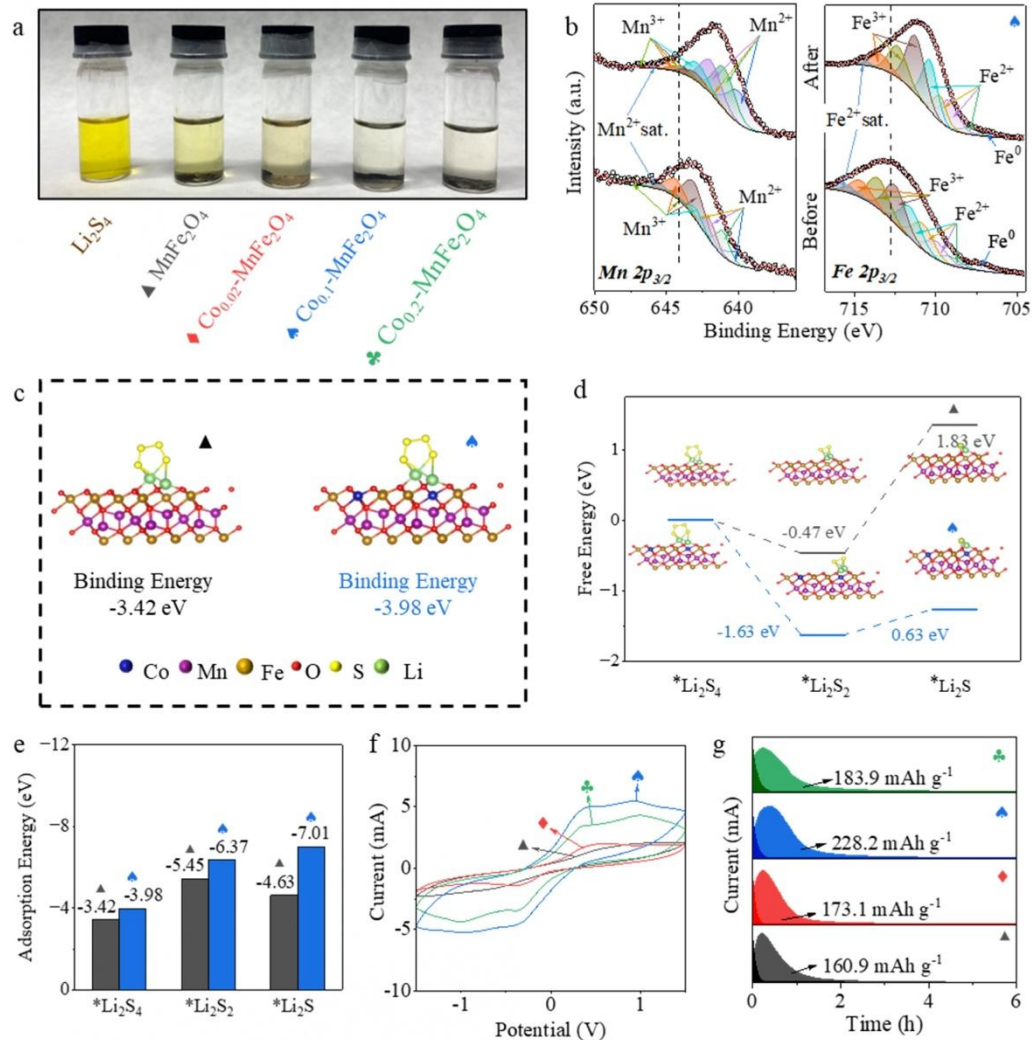


Fig. 2. (a) Optical image of the Li_2S_4 solutions containing the same amount of each adsorber material after 6 h of adsorption. (b) High-resolution Mn $2p_{3/2}$ and Fe $2p_{3/2}$ XPS spectra of $\text{Co}_{0.1}\text{-MnFe}_2\text{O}_4$ before and after Li_2S_4 adsorption. (c) Model of a Li_2S_4 molecule bond on the surface of MnFe_2O_4 and $\text{Co}_{0.1}\text{-MnFe}_2\text{O}_4$. (d) Gibbs free energy profiles of the transformation from Li_2S_4 to Li_2S on the surface of MnFe_2O_4 and $\text{Co}_{0.1}\text{-MnFe}_2\text{O}_4$. (e) Adsorption energy of MnFe_2O_4 and $\text{Co}_{0.1}\text{-MnFe}_2\text{O}_4$ to different sulfur species. (f) CV profiles of symmetric cells at a scan rate of 5 mV s^{-1} . (g) Potentiostatic discharge curves on different electrodes for studying the nucleation kinetics of Li_2S .

(0.63 eV) compared to MnFe_2O_4 (1.83 eV), suggesting that cobalt doping substantially enhances the reaction kinetics by lowering the energy barrier for this critical reaction step. Additionally, the more negative LPS binding energies on the surfaces of MnFe_2O_4 and $\text{Co}_{0.1}\text{-MnFe}_2\text{O}_4$ (Fig. 2e) suggest stronger adsorption of soluble LPS on the latter. These findings align with the conclusion that $\text{Co}_{0.1}\text{-MnFe}_2\text{O}_4$ effectively promotes the adsorption of polysulfides, further supporting its role in improving reaction performance.

To evaluate the ability of the spinel oxides to catalytically accelerate the kinetics of polysulfide conversion, cyclic voltammetry (CV)

measurements on symmetric cells were carried out within a voltage window from -1.5 to 1.5 V using a $0.5 \text{ M Li}_2\text{S}_6$ and 1 M lithium bis (fluoro-methanesulfonyl)imide (LiTFSI) dissolved in DOL/DME (Fig. 2f). At a scan rate of 5 mV s^{-1} , the Co-Mn Fe_2O_4 symmetric cells, particularly $\text{Co}_{0.1}\text{-MnFe}_2\text{O}_4$, show a higher peak current density and larger peak area, indicating more favorable LiPS conversion than undoped MnFe_2O_4 .

The kinetics of the Li_2S nucleation process on the catalyst surfaces were further investigated to evaluate their catalytic activity (Fig. 2g). According to Faraday's law, the capacity (Q) of Li_2S deposition was

calculated as $Q = It$, where I and t are the discharge current and time, respectively. The results show an increasing trend as the cobalt doping content rises, reaching a maximum capacity of 228.2 mAh g^{-1} at approximately 37 min for $\text{Co}_{0.1}\text{-MnFe}_2\text{O}_4$. This indicates that this catalyst provides the highest deposition capacity for Li_2S nucleation.

However, when the cobalt content exceeds 2.4 wt %, the capacity decreases, suggesting that the distribution of cobalt's active sites for Li_2S nucleation reaches a saturation point. Overall, these experimental and theoretical results demonstrate that the conversion of polysulfides to Li_2S is significantly promoted by the presence of Co, which effectively

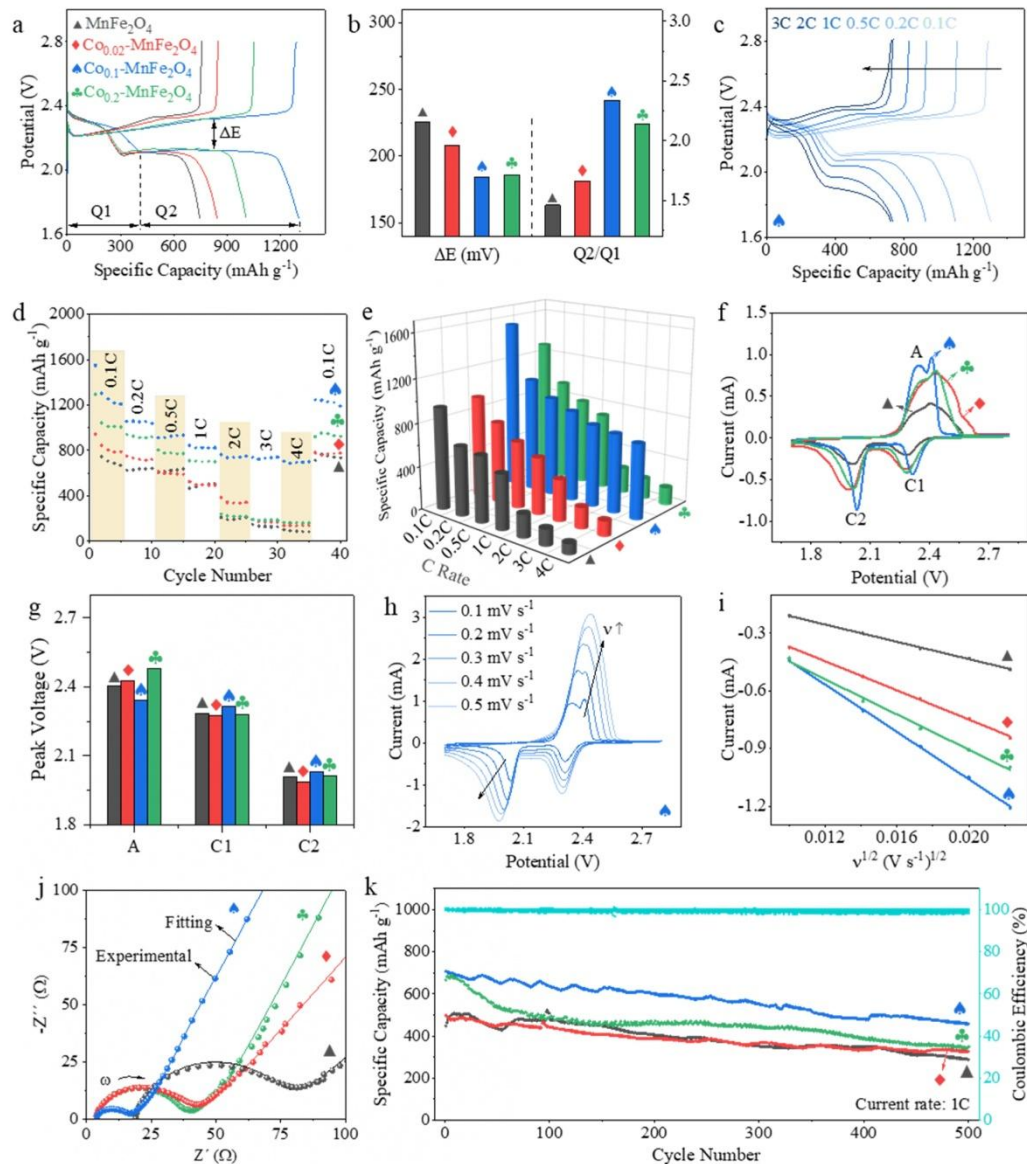


Fig. 3. (a) GCD curves at 0.1C. (b) ΔE and Q_2/Q_1 values obtained from GCD curves. (c) GCD curves of the $\text{Co}_{0.1}\text{-MnFe}_2\text{O}_4/\text{S}$ -based cell at current rates from 0.1C to 3C. (d, e) Rate performance. (f) CV curves of different electrodes at a scan rate of 0.1 mV s^{-1} . (g) Peak voltage obtained from the CV curves. (h) CV profile of the $\text{Co}_{0.1}\text{-MnFe}_2\text{O}_4$ electrode with scan rates (v) ranging from 0.1 to 0.5 mV s^{-1} . (i) CV peaks (C1) current vs. the square root of the scan rate. (j) Nyquist plots of the cells before cycles. (k) Long-term cycling performances at 1 C.

reduces the overpotential of Li_2S nucleation.

Sulfur cathode composites were prepared by combining MnFe_2O_4 or Co-doped MnFe_2O_4 with sulfur (3:7 ratio), sealing the mixture under Ar, and heating it at 155 °C for 24 h. These were blended with high-purity conductive carbon black (Super P), polyvinylidene fluoride (PVDF), and N-methylpyrrolidone (NMP) to create a slurry, which was coated onto aluminum foil, and cut into 12 mm electrodes (see details in the SI). Coin-type cells were assembled using the spinel-modified sulfur cathode ($\text{MnFe}_2\text{O}_4/\text{S}$, $\text{Co}_{0.02}\text{-MnFe}_2\text{O}_4/\text{S}$, $\text{Co}_{0.1}\text{-MnFe}_2\text{O}_4/\text{S}$, and $\text{Co}_{0.2}\text{-MnFe}_2\text{O}_4/\text{S}$), lithium foil as anode, and a solution of 1.0 M LiTFSI and 0.2 M LiNO_3 in DOL/DME as electrolyte. Fig. 3a shows the galvanostatic charge-discharge (GCD) profiles of the four different cells at 0.1 C. All GCD curves show two discharge and one charge plateaus, consistent with the CV measurement results. All the Co-MnFe₂O₄-based cells displayed significantly higher capacities and lower polarization potentials than the MnFe_2O_4 -based cell (Fig. 3a, b). In particular, the $\text{Co}_{0.1}\text{-MnFe}_2\text{O}_4$ -based cell exhibited the highest capacity, at 1302 mAh g⁻¹, and the lowest polarization potential at 184 mV.

The GCD profiles of the $\text{MnFe}_2\text{O}_4/\text{S}$, $\text{Co}_{0.02}\text{-MnFe}_2\text{O}_4/\text{S}$, $\text{Co}_{0.1}\text{-MnFe}_2\text{O}_4/\text{S}$, and $\text{Co}_{0.2}\text{-MnFe}_2\text{O}_4/\text{S}$ -based cells at different rates and their rate performance are displayed in Figs. 3c and S9. The $\text{Co}_{0.1}\text{-MnFe}_2\text{O}_4/\text{S}$ cell displays a remarkable rate capability, delivering capacities of 1303 to 693 mAh g⁻¹ at 0.1 C, 0.2 C, 0.5 C, 1.0 C, 2.0 C, 3.0 C, and 4.0 C, outperforming the electrochemical activities of MnFe_2O_4 , $\text{Co}_{0.02}\text{-MnFe}_2\text{O}_4$, and $\text{Co}_{0.2}\text{-MnFe}_2\text{O}_4$. When the rate was returned to 0.1C, the specific capacity maintained a value of 1245 mAh g⁻¹, demonstrating the excellent rate performance of the $\text{Co}_{0.1}\text{-MnFe}_2\text{O}_4$ -based electrode. In addition, $\text{Co}_{0.1}\text{-MnFe}_2\text{O}_4/\text{S}$ cathodes demonstrate superior specific capacity performance at 0.5 C when compared to previous reports on spinel-structured sulfur host materials, particularly noteworthy given the absence of any porous or high surface area support in the present study.

Fig. 3f exhibits the CV curves of $\text{MnFe}_2\text{O}_4/\text{S}$, $\text{Co}_{0.02}\text{-MnFe}_2\text{O}_4/\text{S}$, $\text{Co}_{0.1}\text{-MnFe}_2\text{O}_4/\text{S}$, and $\text{Co}_{0.2}\text{-MnFe}_2\text{O}_4/\text{S}$ -based LSB coin cells (1.0 M LiTFSI in DOL/DME with 0.2 M LiNO_3 electrolyte) at a scan rate of 0.1 mV s⁻¹ and in the voltage range 1.7 to 2.8 V. All curves show two cathodic peaks (C_1 and C_2) and one anodic peak (A). The two cathodic peaks account for the reduction of S_8 to high-order LiPS (Li_2S_x , $4 \leq x \leq 8$), and their subsequent transformation to low-order $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$, respectively. The oxidation peak was related to the transformation of Li_2S to S_8 . Among the tested cathode materials, $\text{Co}_{0.1}\text{-MnFe}_2\text{O}_4/\text{S}$ exhibits the highest current densities and the most favorable reduction and oxidation peak potentials, with the highest/lowest cathodic/anodic peak voltages and onset potentials, indicating superior redox reaction kinetics (Fig. 3g and S10). Moreover, Figure S11 presents the polarization curves and corresponding Tafel plots from the oxidation (A) and reduction peaks (C_1 and C_2) observed in the CV curves. The $\text{Co}_{0.1}\text{-MnFe}_2\text{O}_4$ sample exhibited significantly lower slopes at each peak ($A_1 = 55.6 \text{ mV dec}^{-1}$, $C_1 = 76.3 \text{ mV dec}^{-1}$, and $C_2 = 101.3 \text{ mV dec}^{-1}$) compared to the other samples. This highlights the enhanced reaction kinetics achieved with the optimized Co substitution.

CV curves at different rates from 0.1 to 0.5 mV s⁻¹ were used to analyze the Li^+ -ion diffusion ability within the different host materials (Figs. 3h and S12). The Li^+ diffusion coefficient was calculated according to the Randles-Sevcik equation.

$$I_p = [(2.69 \times 10^5) \times n^{1.5} \times A \times D_{\text{Li}^+}^{0.5} \times C_{\text{Li}^+} \times v^{0.5}] \quad (1)$$

where I_p is the peak current, n is the number of charges involved in the reaction, A is the geometric electrode area, C_{Li^+} is the concentration of Li^+ ion in the cathode, and v is the sweep rate. As shown in Fig. 3i, the $\text{Co}_{0.1}\text{-MnFe}_2\text{O}_4/\text{S}$ cathode provided the highest I_p vs. $v^{1/2}$ slope compared with $\text{MnFe}_2\text{O}_4/\text{S}$, $\text{Co}_{0.02}\text{-MnFe}_2\text{O}_4/\text{S}$, and $\text{Co}_{0.2}\text{-MnFe}_2\text{O}_4/\text{S}$, corresponding to the highest D_{Li^+} values determined from the two cathodic and the anodic peak, at 2.03×10^{-7} , 2.46×10^{-7} , and $5.74 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, respectively (Figure S13).

Electrochemical impedance spectroscopy (EIS) was employed to further qualitatively evaluate the charge transfer resistance (R_{ct}) and Li^+ diffusion capability. As shown in the Nyquist plot in Fig. 3j, the $\text{Co}_{0.1}\text{-MnFe}_2\text{O}_4/\text{S}$ sample exhibited the smallest semicircle at high frequencies (ω) and the steepest slope in the low-frequency region, indicating faster charge transfer kinetics and enhanced Li^+ diffusion compared to the samples evaluated, which is consistent with the Li^+ diffusion coefficient calculated from the CV curves [51]. Analysis of the Nyquist plot data, interpreted using the equivalent circuit model displayed in Figure S14 shows the $\text{Co}_{0.1}\text{-MnFe}_2\text{O}_4$ sample to have the lowest R_{ct} (16.1 Ω) compared to $\text{MnFe}_2\text{O}_4/\text{S}$ (80.5 Ω), $\text{Co}_{0.02}\text{-MnFe}_2\text{O}_4/\text{S}$ (42.4 Ω), and $\text{Co}_{0.2}\text{-MnFe}_2\text{O}_4/\text{S}$ (38.8 Ω).

EIS measurements of coin cells after 100 GCD cycles at 0.5C show an increase in the R_{ct} in all the samples tested, which is associated with the deposition of insulating discharge products ($\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$) on the electrode surface during cycling [51,52]. Additionally, after 100 cycles, the emergence of a second semicircle is observed (Figure S15a). This is attributed to the formation of a new interface associated with a polysulfide deposition layer on the cathode and was modelled by introducing an R_p -CPE element in the equivalent circuit (Figure S15b). The $\text{Co}_{0.1}\text{-MnFe}_2\text{O}_4/\text{S}$ sample consistently exhibited the lowest R_{ct} (Figure S15c) compared to the other samples, indicating faster polysulfide conversion with more efficient charger transfer kinetics during lithiation and delithiation [26]. Additionally, the $\text{Co}_{0.1}\text{-MnFe}_2\text{O}_4/\text{S}$ sample showed a lower R_p (Figure S15d), which is correlated with a reduced LiPS deposition layer related to a more reversible reaction mechanism [53,54].

To evaluate the cycling stability of LSBs with different cathodes, GCD tests for 200 cycles at a fixed current of 0.5C were carried out. Figure S16 shows that cells with $\text{Co}_{0.1}\text{-MnFe}_2\text{O}_4/\text{S}$ deliver higher initial specific discharge capacities (898 mAh g⁻¹) than $\text{MnFe}_2\text{O}_4/\text{S}$ (598 mAh g⁻¹), $\text{Co}_{0.02}\text{-MnFe}_2\text{O}_4/\text{S}$ (622 mAh g⁻¹), and $\text{Co}_{0.2}\text{-MnFe}_2\text{O}_4/\text{S}$ (770 mAh g⁻¹). After 100 cycles, the decay rate of $\text{Co}_{0.1}\text{-MnFe}_2\text{O}_4/\text{S}$ electrode is 0.031 % per cycle. In contrast, the decay rate of $\text{MnFe}_2\text{O}_4/\text{S}$, $\text{Co}_{0.02}\text{-MnFe}_2\text{O}_4/\text{S}$, and $\text{Co}_{0.2}\text{-MnFe}_2\text{O}_4/\text{S}$ electrodes are 0.105, 0.327, and 0.309 % per cycle.

Longer-term stability performance of the $\text{MnFe}_2\text{O}_4/\text{S}$, $\text{Co}_{0.02}\text{-MnFe}_2\text{O}_4/\text{S}$, $\text{Co}_{0.1}\text{-MnFe}_2\text{O}_4/\text{S}$, and $\text{Co}_{0.2}\text{-MnFe}_2\text{O}_4/\text{S}$ cells was investigated at 1C (Fig. 3k). Compared with $\text{MnFe}_2\text{O}_4/\text{S}$, $\text{Co}_{0.02}\text{-MnFe}_2\text{O}_4/\text{S}$, and $\text{Co}_{0.2}\text{-MnFe}_2\text{O}_4/\text{S}$, $\text{Co}_{0.1}\text{-MnFe}_2\text{O}_4/\text{S}$ shows a higher initial capacity. In addition, $\text{Co}_{0.1}\text{-MnFe}_2\text{O}_4/\text{S}$ also exhibits a higher capacity retention of 65.7 % after 500 cycles compared to $\text{MnFe}_2\text{O}_4/\text{S}$ (56.6 %), $\text{Co}_{0.02}\text{-MnFe}_2\text{O}_4/\text{S}$ (64.3 %) and $\text{Co}_{0.2}\text{-MnFe}_2\text{O}_4/\text{S}$ (51.4 %). Furthermore, the self-discharge performance of $\text{Co}_{0.1}\text{-MnFe}_2\text{O}_4/\text{S}$ was evaluated by cycling the battery for 10 cycles and then leaving it charged to rest for 76 h before resuming cycling (Figure S17). Capacity retention was defined as the ratio between the charge in the 10th cycle and the discharge capacity obtained after the 76-hour rest. The capacity lost during the 76-hour rest was 36.6 %, resulting in a self-discharge of 0.482 % per hour.

To evaluate the practical potential of LSBs with $\text{Co}_{0.1}\text{-MnFe}_2\text{O}_4$ -based electrodes, cells were assembled with higher sulfur loadings. Fig. 4a shows the GCD profiles at 0.1C of $\text{Co}_{0.1}\text{-MnFe}_2\text{O}_4$ -based cells having sulfur loadings of 2.3 and 3 mg cm⁻². The cells delivered specific capacities of 845 and 597 mAh g⁻¹ after 100 cycles, respectively. Additionally, the corresponding GCD profiles exhibit clearly defined plateaus, which align with the superior catalytic performance of $\text{Co}_{0.1}\text{-MnFe}_2\text{O}_4$ (Fig. 4b). Finally, to showcase practical utility, a 2025-type coin cell assembled using a $\text{Co}_{0.1}\text{-MnFe}_2\text{O}_4/\text{S}$ cathode was demonstrated to power a lab timer, highlighting the real-world application of the fabricated electrode (Fig. 4c).

According to the reported octahedral site preference energy (OSPE), Co^{2+} exhibits a higher absolute energy value (31 kJ mol⁻¹) compared to Mn^{2+} and Fe^{3+} (0 kJ mol⁻¹ in both instances), indicating that Co^{2+} has a stronger preference for occupying octahedral interstices by substituting Fe^{3+} ions [50]. Considering this structure, additional DFT calculations were conducted to elucidate the role of Co and its content in MnFe_2O_4 .

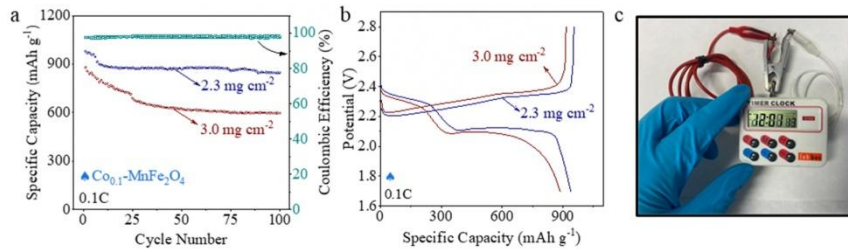


Fig. 4. (a) Cycling performances of $\text{Co}_{0.1}\text{-MnFe}_2\text{O}_4/\text{S}$ -based cells having sulfur loadings of 2.3 and 3.0 mg cm^{-2} at 0.1C. (b) GCD curves at 0.1C. (c) A $\text{Co}_{0.1}\text{-MnFe}_2\text{O}_4/\text{S}$ -based coin cell powering a lab timer.

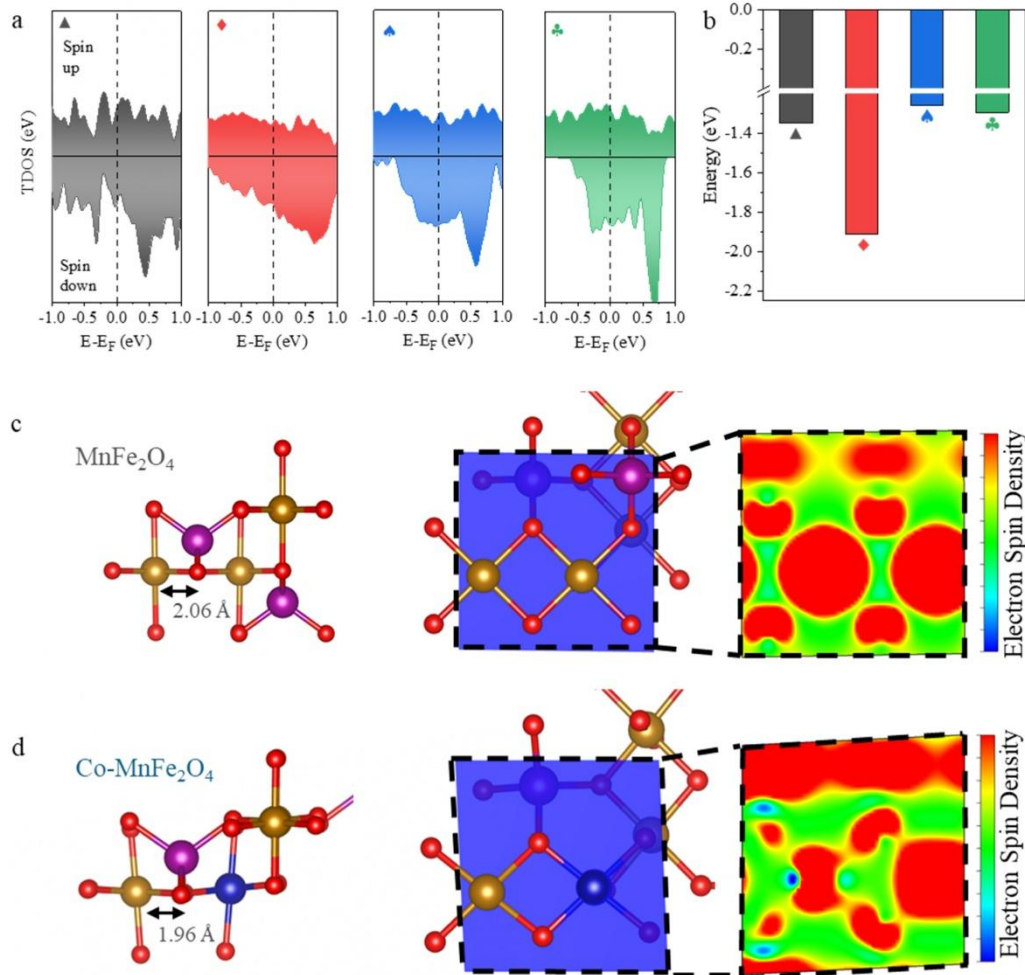


Fig. 5. (a) TDOS of MnFe_2O_4 (▲), $\text{Co}_{0.02}\text{-MnFe}_2\text{O}_4$ (◆), $\text{Co}_{0.1}\text{-MnFe}_2\text{O}_4$ (♣), $\text{Co}_{0.2}\text{-MnFe}_2\text{O}_4$ (♠) and (b) a comparison of the energy d-band center for the tested sample set. DFT schematic representation of Fe-O octahedron bond distance and 2D spin electron density in (c) MnFe_2O_4 and (d) $\text{Co-MnFe}_2\text{O}_4$.

Fig. 5a displays the total density of states (TDOS) of MnFe_2O_4 , $\text{Co}_{0.02}\text{-MnFe}_2\text{O}_4$, $\text{Co}_{0.1}\text{-MnFe}_2\text{O}_4$ and $\text{Co}_{0.2}\text{-MnFe}_2\text{O}_4$ lattice models (Figure S18). These models were generated considering a random Co^{2+} substitution at the octahedral site of the spinel structure, initially occupied by Fe^{3+} . Samples with approximate Co weight ratios of 0.5 % ($\text{Co}_{0.02}\text{-MnFe}_2\text{O}_4$), 2.4 % ($\text{Co}_{0.1}\text{-MnFe}_2\text{O}_4$), and 4.8 % ($\text{Co}_{0.2}\text{-MnFe}_2\text{O}_4$) were qualitatively evaluated. Among these, $\text{Co}_{0.1}\text{-MnFe}_2\text{O}_4$ shows the d -band center energy closest to the Fermi level (Fig. 5b), indicating enhanced charge transport and an increased likelihood of electrons populating the antibonding orbitals between the material and adsorbed sulfur species [55–59]. The molecular model obtained through DFT further reveals that Co-doping results in a shortening of the Fe–O bond length (Fig. 5c and d), which is consistent with XRD and HRTEM findings. This structural change promotes orbital hybridization, which is evidenced by the d -band center shifting closer to the Fermi level. Compared to the 2D spin electron density of MnFe_2O_4 , the lattice distortions induced by Co-doping are clearly visible in Fig. 5d, where electron density delocalization is observed among Fe–O and Co–O bonds, resulting from bonding hydronation.

3. Conclusion

To summarize, Co-doped MnFe_2O_4 particles synthesized using a hydrothermal method showed significant promise as sulfur redox catalysts in LSBs. The introduction of small amounts of cobalt into the MnFe_2O_4 structure facilitates the hybridization of Fe–O and Co–O orbitals. This alteration brings the d -band center closer to the Fermi level, which enhances charge transport and transfer properties, crucial for improving the electrocatalytic performance of the battery. Optimizing the cobalt doping level to just 2.4 wt % not only maximizes these benefits but also results in a material that exhibits a high initial capacity (1302 mAh g^{-1}), excellent rate capability, and sustained cycle life, even under high sulfur loading conditions. This research underscores the effectiveness of strategic doping to modify the surface-active sites of spinel oxides, thereby enhancing their interaction with LiPSs during battery operation. The careful adjustment of cobalt levels helps regulate the adsorption of LiPS reactions, which is key for minimizing the common challenges of polysulfide shuttling and improving the overall stability and efficiency of LSBs.

CRedit authorship contribution statement

Jesús Chacón-Borrero: Writing – original draft, Methodology, Investigation, Formal analysis. **Xuede Qi:** Writing – original draft, Methodology, Investigation. **Xuesong Zhang:** Formal analysis. **Armando Berlanga-Vázquez:** Formal analysis. **Xingqi Chang:** Formal analysis. **Guillem Montaña-Mora:** Formal analysis. **Karol V. Mejía-Centeno:** Formal analysis. **Helena Rabelo Freitas:** Formal analysis. **Maria Chiara Spadaro:** Formal analysis. **Jordi Arbiol:** Formal analysis. **Jordi Llorca:** Formal analysis. **Pablo Guardia:** Formal analysis. **Xueqiang Qi:** Formal analysis. **Chao Yue Zhang:** Writing – review & editing, Investigation. **Andreu Cabot:** Writing – review & editing, Supervision, Resources.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.ensm.2025.104207](https://doi.org/10.1016/j.ensm.2025.104207).

References

- [1] T. Gül, A.F. Pales, E. Connelly, Global EV outlook 2024 moving towards increased affordability, 2024. www.ica.org.
- [2] J.T. Frith, M.J. Lacey, U. Ulissi, A non-academic perspective on the future of lithium-based batteries, *Nat. Commun.* 14 (2023) 420, <https://doi.org/10.1038/s41467-023-35933-2>.
- [3] F.M.N.U. Khan, M.G. Rasul, A.S.M. Sayem, N. Mandal, Maximizing energy density of lithium-ion batteries for electric vehicles: a critical review, *Energy Reports* 9 (2023) 11–21, <https://doi.org/10.1016/j.egyr.2023.08.069>.
- [4] J. Xu, X. Cai, S. Cai, Y. Shao, C. Hu, S. Lu, S. Ding, <sc>high-energy</sc>sc>lithium-ion batteries: recent progress and a promising future in applications, *ENERGY Environ. Mater.* 6 (2023) e12450, <https://doi.org/10.1002/enn2.12450>.
- [5] E. Muchuweni, E.T. Mombeshora, C.M. Muiva, T.S. Sathiaraj, Towards high-performance lithium-ion batteries by introducing graphene based materials into LiFePO_4 cathodes: a review, *Nano Trends* 6 (2024) 100034, <https://doi.org/10.1016/j.nmnt.2024.100034>.
- [6] Z. Ye, J. Li, Z. Li, Recent progress in nonflammable electrolytes and cell design for safe Li-ion batteries, *J. Mater. Chem. A* 11 (2023) 15576–15599, <https://doi.org/10.1039/d3ta01951a>.
- [7] S. Hasselwander, M. Meyer, I. Österle, Techno economic analysis of different battery cell chemistries for the passenger vehicle market, *Batteries* 9 (2023) 379, <https://doi.org/10.3390/batteries9070379>.
- [8] G. Zhou, H. Chen, Y. Cui, Formulating energy density for designing practical lithium-sulfur batteries, *Nat. Energy* 7 (2022) 312–319, <https://doi.org/10.1038/s41560-022-01001-0>.
- [9] G. Benveniste, A. Sánchez, H. Rallo, C. Corchero, B. Amante, Comparative life cycle assessment of Li sulphur and Li ion batteries for electric vehicles, *Resour. Conserv. Recycl. Adv.* 15 (2022) 200086, <https://doi.org/10.1016/j.rcradv.2022.200086>.
- [10] R. Wang, R. Wu, X. Yan, D. Liu, P. Guo, W. Li, H. Pan, Implanting single Zn atoms coupled with metallic Co nanoparticles into porous carbon nanosheets grafted with carbon nanotubes for high-performance lithium-sulfur batteries, *Adv. Funct. Mater.* 32 (2022) 2200424, <https://doi.org/10.1002/adfm.202200424>.
- [11] R. Wang, R. Wu, C. Ding, Z. Chen, H. Xu, Y. Liu, J. Zhang, Y. Ha, B. Fei, H. Pan, Porous carbon architecture assembled by cross-linked carbon leaves with implanted atomic cobalt for high-performance Li-S batteries, *Nano-Micro Lett* 13 (2021) 151, <https://doi.org/10.1007/s40820-021-00676-6>.
- [12] J. Jiao, D. Liu, Y. He, Y. Shen, J. Zhou, C. Liang, H. Pan, R. Wu, Entropy engineering modulated d-band center of transition metal nitrides for catalyzing polysulfide conversion in lithium-sulfur batteries, *Small* (2024) 2409740, <https://doi.org/10.1002/smll.202409740>.
- [13] R. Wang, J. Jiao, D. Liu, Y. He, Y. Yang, D. Sun, H. Pan, F. Fang, R. Wu, High-entropy metal nitride embedded in concave porous carbon enabling polysulfide conversion in lithium-sulfur batteries, *Small* 20 (2024) 2405148, <https://doi.org/10.1002/smll.202405148>.
- [14] Y. Fei, G. Li, Unveiling the pivotal parameters for advancing high energy density in lithium-sulfur batteries: a comprehensive review, *Adv. Funct. Mater.* 34 (2024) 2312550, <https://doi.org/10.1002/adfm.202312550>.

- [15] M. Waqas, Y. Niu, M. Tang, Y. Pang, S. Ali, Y. Dong, W. Lv, W. He, A decade of development in cathode-facing surface modified separators for high-performance Li-S batteries, *Energy Storage Mater* 72 (2024) 103682, <https://doi.org/10.1016/j.ensm.2024.103682>.
- [16] A. Rafie, J.W. Kim, K.K. Sarode, V. Kalra, A review on the use of carbonate-based electrolytes in Li-S batteries: a comprehensive approach enabling solid-solid direct conversion reaction, *Energy Storage Mater* 50 (2022) 197–224, <https://doi.org/10.1016/j.ensm.2022.03.015>.
- [17] Z.C. Lv, P.F. Wang, J.C. Wang, S.H. Tian, T.F. Yi, Key challenges, recent advances and future perspectives of rechargeable lithium-sulfur batteries, *J. Ind. Eng. Chem.* 124 (2023) 68–88, <https://doi.org/10.1016/j.jiec.2023.04.025>.
- [18] N. Nakamura, S. Ahi, T. Momma, T. Osaka, Future potential for lithium-sulfur batteries, *J. Power Sources* 558 (2023) 232566, <https://doi.org/10.1016/j.jpowsour.2022.232566>.
- [19] K.R. Nagde, S.J. Dhoble, Li-S ion batteries: a substitute for Li-ion storage batteries. *Energy Mater.*, Elsevier, 2021, pp. 335–371, <https://doi.org/10.1016/B978-0-12-823710-6.00008-X>.
- [20] W. Qi, J. Xia, C. Luo, C. Zhang, R. Chen, W. Lv, Q. Yang, Lithium-sulfur batteries at extreme temperatures: challenges, strategies and prospects, *Energy Environ. Mater.* 6 (2023) e12444, <https://doi.org/10.1002/eenm.12444>.
- [21] M. Manimehali, P. Saranya, T. Theivasanthi, S.C.B. Gopinath, Sulphur/functionalized graphene composite as cathode for improved performance and life cycle of lithium-sulphur batteries, *Chem. Eng. J.* 496 (2024) 154349, <https://doi.org/10.1016/j.cej.2024.154349>.
- [22] Y. Jin, N. Deng, Y. Li, H. Wang, M. Zhang, W. Kang, B. Cheng, Advanced preparation and application of bimetallic materials in lithium sulfur batteries: a review, *J. Energy Chem.* 88 (2024) 469–512, <https://doi.org/10.1016/j.jechem.2023.09.031>.
- [23] W. Jan, A.D. Khan, F.J. Iftikhar, G. Ali, Recent advancements and challenges in deploying lithium sulfur batteries as economical energy storage devices, *J. Energy Storage* 72 (2023) 108559, <https://doi.org/10.1016/j.est.2023.108559>.
- [24] S. Dong, H. Liu, Y. Hu, S. Chong, Cathode materials for rechargeable lithium-sulfur batteries: current progress and future prospects, *ChemElectroChem* 9 (2022) e202101564, <https://doi.org/10.1002/celec.202101564>.
- [25] X. Kang, T. He, R. Zou, S. Niu, Y. Ma, F. Zhu, F. Ran, Size effect for inhibiting polysulfides shuttle in lithium-sulfur batteries, *Small* 20 (2024) e2306503, <https://doi.org/10.1002/smll.202306503>.
- [26] C. Zhang, R. Du, J.J. Biendicho, M. Yi, K. Xiao, D. Yang, T. Zhang, X. Wang, J. Arbiol, J. Llorca, Y. Zhou, J.R. Morante, A. Cabot, Tubular CoFeP@CN as a Mott-Schottky catalyst with multiple adsorption sites for robust lithium-sulfur batteries, *Adv. Energy Mater.* 11 (2021) 2100432, <https://doi.org/10.1002/aenm.202100432>.
- [27] C. Zhang, J.J. Biendicho, T. Zhang, R. Du, J. Li, X. Yang, J. Arbiol, Y. Zhou, J. R. Morante, A. Cabot, Combined high catalytic activity and efficient polar tubular nanostructure in urchin-like metallic NiCo₂Se₄ for high-performance lithium-sulfur batteries, *Adv. Funct. Mater.* 29 (2019) 1903842, <https://doi.org/10.1002/adfm.201903842>.
- [28] H. Pan, Z. Cheng, Z. Zhou, S. Xie, W. Zhang, N. Han, W. Guo, J. Franssaer, J. Luo, A. Cabot, M. Wübbenhorst, Boosting lean electrolyte lithium-sulfur battery performance with transition metals: a comprehensive review, *Nano Micro Lett* 15 (2023) 165, <https://doi.org/10.1007/s40820-023-01137-y>.
- [29] C.Y. Zhang, L. Gong, C. Zhang, X. Cheng, L. Balcells, G. Zeng, J.J. Biendicho, J. Li, G.Z. Sun, J.Y. Zhou, A. Cabot, Sodium sulfur batteries with unprecedented capacity, cycling stability and operation temperature range enabled by a CoFe₂O₄ catalytic additive under an external magnetic field, *Adv. Funct. Mater.* 33 (2023) 2305908, <https://doi.org/10.1002/adfm.202305908>.
- [30] C.Y. Zhang, X. Lu, X. Han, J. Yu, C. Zhang, C. Huang, L. Balcells, A.G. Marjón, J. Jacas Biendicho, J. Li, J. Arbiol, G. Sun, J.Y. Zhou, A. Cabot, Identifying the role of the cationic geometric configuration in spinel catalysts for polysulfide conversion in sodium-sulfur batteries, *J. Am. Chem. Soc.* 145 (2023) 18992–19004, <https://doi.org/10.1021/jacs.3c06288>.
- [31] M. Bi, S. Yao, C. Zhang, H. Yu, X. Zhang, H. Liu, T. Zhang, X. Shen, Hybrid of spinel zinc-cobalt oxide nanospheres combined with nitrogen-containing carbon nanofibers as advanced electrocatalyst for redox reaction in lithium/polysulfides batteries, *Adv. Powder Technol.* 33 (2022) 103710, <https://doi.org/10.1016/j.appt.2022.103710>.
- [32] Mingzhu Bi, M. Chao, C. Zhang, H. Yu, X. Zhang, H. Liu, T. Zhang, J. Mi, X. Shen, S. Yao, Self assembled flower like structure of copper cobaltate nanosheets supported on nitrogen-doped carbon nanofibers as functional electrocatalyst for lithium/polysulfides batteries Mingzhu, *J. Alloys Compd.* 934 (2023) 167916, <https://doi.org/10.1016/j.jallcom.2005.05.002>.
- [33] X. Huang, P. Zeng, Y. Lu, J. Yang, M. Chen, H. Liu, X. Wang, Revealing the role of crystal structure to catalysis: inverse spinel phase Co-Mn-based catalyst for Li-S batteries, *Chem. Eng. J.* 487 (2024) 150490, <https://doi.org/10.1016/j.cej.2024.150490>.
- [34] Y. Jiang, H.M.U. Arshad, H.-J. Li, S. Liu, G. Li, X. Gao, Crystalline multi-metallic compounds as host materials in cathode for lithium-sulfur batteries, *Small* 17 (2021) e2005332, <https://doi.org/10.1002/smll.202005332>.
- [35] X. Zhu, A. Huang, I. Martens, N. Vostrov, Y. Sun, M. Richard, T.U. Schüll, L. Wang, High-voltage spinel cathode materials: navigating the structural evolution for lithium ion batteries, *Adv. Mater.* 36 (2024) 2403482, <https://doi.org/10.1002/adma.202403482>.
- [36] H. Li, P. Shi, L. Wang, T. Yan, T. Guo, X. Xia, C. Chen, J. Mao, D. Sun, L. Zhang, Cooperative catalysis of polysulfides in lithium sulfur batteries through adsorption competition by tuning cationic geometric configuration of dual-active sites in spinel oxides, *Angew. Chem. Int. Ed. Engl.* 62 (2023) e202216286, <https://doi.org/10.1002/anie.202216286>.
- [37] É.A. Santos, C.G. Anchieta, R.C. Fernandes, M.J. Pinzón, C. A.N. Miranda, I. Galantini, F.C.B. Maia, G. Doubek, C.B. Rodella, L.M. Da Silva, H. Zanin, Combining in situ electrochemistry, operando FTIR and post-mortem analyses to understand Co-Mn-Al spinels on mitigating shuttle effect in lithium-sulfur battery, *Nano Energy* 116 (2023) 108809, <https://doi.org/10.1016/j.nanoen.2023.108809>.
- [38] Y. Deng, J. Yang, Z. Qiu, W. Tang, Y. Li, Q. Wang, R. Liu, NiS/NiCo₂O₄ cooperative interfaces enable fast sulfur redox kinetics for lithium-sulfur battery, *Small Methods* 8 (2024) 2301316, <https://doi.org/10.1002/smtd.202301316>.
- [39] C. Huang, J. Yu, C. Li, Z. Cui, C. Zhang, C. Zhang, B. Nan, J. Li, J. Arbiol, A. Cabot, Combined defect and heterojunction engineering in ZnTe/CoTe₂@NC Sulfur hosts toward robust lithium-sulfur batteries, *Adv. Funct. Mater.* 33 (2023) 2305624, <https://doi.org/10.1002/adfm.202305624>.
- [40] K. Wu, H. He, Q. Xue, C. Zhang, X. Qi, A. Cabot, X. Hu, CoSe₂ decorated carbon nanofibers: a catalytic electrode for uniform Li₂Se nucleation in lithium-selenium batteries, *Chem. Eng. J.* 466 (2023) 142988, <https://doi.org/10.1016/j.cej.2023.142988>.
- [41] C. Zhao, F. Huo, Y. Yang, J. Ruan, F. Chai, H. Xu, Y. Liu, L. Zhang, A. Cabot, Z. Sun, Y. Zhang, Development of synergistically efficient Ni-Co pair catalytic sites for enhanced polysulfide conversion in lithium-sulfur batteries, *Adv. Funct. Mater.* 34 (2024) 2402175, <https://doi.org/10.1002/adfm.202402175>.
- [42] C. Huang, J. Yu, Y.J. Lei, O. Usoltsev, L. Gong, Z. Cui, J. Li, C. Li, B. Nan, X. Lu, R. He, X. Qi, Q. Xue, J. Chai, Y. Ren, X. Bi, Y. Cheng, J.Y. Zhou, A. Skorynina, A. Bugaev, P.R. Martínez Alanis, L. Balcells, J. Arbiol, C.Y. Zhang, A. Cabot, Generation of unpaired electrons to promote electron transfer at the cathode of room-temperature sodium sulfur batteries, *Chem. Eng. J.* 506 (2025) 160146, <https://doi.org/10.1016/j.cej.2025.160146>.
- [43] D. Yang, J. Wang, C. Lou, M. Li, C. Zhang, A. Ramon, C. Li, M. Tang, G. Henkelman, M. Xu, J. Li, J. Llorca, J. Arbiol, D. Mitlin, G. Zhou, A. Cabot, Single-atom catalysts with unsaturated Co-N₂ active sites based on a C₂N 2D-organic framework for efficient sulfur redox reaction, *ACS Energy Lett* 9 (2024) 2083–2091, <https://doi.org/10.1021/acscenergylett.4c00771>.
- [44] J. Yu, C. Huang, O. Usoltsev, A.P. Black, K. Gupta, M.C. Spadaro, I. Pinto-Huguet, M. Botifoll, C. Li, J. Herrero-Martín, J. Zhou, A. Ponrouch, R. Zhao, L. Balcells, C. Y. Zhang, A. Cabot, J. Arbiol, Promoting polysulfide redox reactions through electronic spin manipulation, *ACS Nano* 18 (2024) 19268–19282, <https://doi.org/10.1021/acsnano.4c05278>.
- [45] R. Xiao, D. Luo, J. Wang, H. Lu, H. Ma, E.M. Akinoglu, M. Jin, X. Wang, Y. Zhang, Z. Chen, Oxidation states regulation of cobalt active sites through crystal surface engineering for enhanced polysulfide conversion in lithium sulfur batteries, *Adv. Sci. (Weinheim, Baden-Württemberg, Ger.)* 9 (2022) e2202352, <https://doi.org/10.1002/advs.202202352>.
- [46] J. Wang, W. Han, A review of heteroatom doped materials for advanced lithium-sulfur batteries, *Adv. Funct. Mater.* 32 (2022) 2107166, <https://doi.org/10.1002/adfm.202107166>.
- [47] W. Liu, C. Luo, S. Zhang, B. Zhang, J. Ma, X. Wang, W. Liu, Z. Li, Q.H. Yang, W. Lv, Cobalt doping of molybdenum disulfide for enhanced catalytic polysulfide conversion in lithium-sulfur batteries, *ACS Nano* 15 (2021) 7491–7499, <https://doi.org/10.1021/acsnano.1c00896>.
- [48] S. Mallick, A. Patel, X.G. Sun, M.P. Paranthaman, M. Mou, J.H. Mugumya, M. Jiang, M.L. Rasche, H. Lopez, R.B. Gupta, Low-cobalt active cathode materials for high-performance lithium-ion batteries: synthesis and performance enhancement methods, *J. Mater. Chem. A* 11 (2023) 3789–3821, <https://doi.org/10.1039/d2ta08251a>.
- [49] J. Ma, J. Wang, K. Jia, Z. Liang, G. Ji, H. Ji, Y. Zhu, W. Chen, H. M. Cheng, G. Zhou, Subtractive transformation of cathode materials in spent Li-ion batteries to a low-cobalt 5 V class cathode material, *Nat. Commun.* 15 (2024) 1046, <https://doi.org/10.1038/s41467-024-45091-8>.
- [50] Q. Zhao, Z. Yan, C. Chen, J. Chen, Spinel: controlled preparation, oxygen reduction/evolution reaction application, and beyond, *Chem. Rev.* 117 (2017) 10121–10211, <https://doi.org/10.1021/acs.chemrev.7b00051>.
- [51] J. Yu, I. Pinto-Huguet, C.Y. Zhang, Y. Zhou, Y. Xu, A. Vizintin, J.J. Velasco-Vélez, X. Qi, X. Pan, G. Oney, A. Olgo, K. Märker, L.M. Da Silva, Y. Luo, Y. Lu, C. Huang, E. Härk, J. Fleming, P. Chenevier, A. Cabot, Y. Bai, M. Botifoll, A.P. Black, Q. An, T. Amietszajew, J. Arbiol, Mechanistic insights and technical challenges in sulfur-based batteries: a comprehensive In situ/operando monitoring toolbox, *ACS Energy Lett.* (2024) 6178–6214, <https://doi.org/10.1021/acscenergylett.4c02703>.
- [52] C. Li, J. Yu, C. Zhang, D. Yang, J. Wang, H. Li, C. Huang, K. Xiao, Y. Cheng, Y. Ren, X. Qi, T. Yang, J. Li, J. Wang, G. Henkelman, J. Arbiol, J. Nan, A. Cabot, Tungsten phosphide on nitrogen and phosphorus doped carbon as a functional membrane coating enabling robust lithium-sulfur batteries, *J. Colloid Interface Sci.* 670 (2024) 61–72, <https://doi.org/10.1016/j.jcis.2024.05.074>.
- [53] M.V. Bracamonte, A. Vizintin, G. Kapun, F. Conetto, J. Bitenc, A. Randon Vitanova, M. Gabersček, R. Dominko, Surface film formation on Mg electrode containing magnesium polysulfides in TFSI-based electrolytes, *J. Power Sources* 555 (2023) 232367, <https://doi.org/10.1016/j.jpowsour.2022.232367>.
- [54] F. Zhao, Y. Zhao, J. Wang, Q. Sun, K. Adair, S. Zhang, J. Luo, J. Li, W. Li, Y. Sun, X. Li, J. Liang, C. Wang, R. Li, H. Huang, L. Zhang, S. Zhao, S. Lu, X. Sun, Tuning bifunctional interface for advanced sulfide based all solid state batteries, *Energy Storage Mater* 33 (2020) 139–146, <https://doi.org/10.1016/j.ensm.2020.06.013>.
- [55] C. Huang, J. Yu, C.Y. Zhang, Z. Cui, J. Chen, W. Lai, Y. Lei, B. Nan, X. Lu, R. He, L. Gong, J. Li, C. Li, X. Qi, Q. Xue, J.Y. Zhou, X. Qi, L. Balcells, J. Arbiol, A. Cabot, Electronic spin alignment within homologous NiS₂/NiSe₂ heterostructures to

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Energy Storage Materials 77 (2025) 104207

- promote sulfur redox kinetics in lithium-sulfur batteries, *Adv. Mater.* 36 (2024) 2400810, <https://doi.org/10.1002/adma.202400810>.
- [56] W. Bi, C. Li, D. Yang, Y.Z. Zhang, L. Hu, Q. Gong, J. Zhang, Y. Zhang, M. Li, J. Wei, Y. Zhou, D. Zhou, T. Wu, L.F. Chen, A. Cabot, MOF-derived ultrathin carbon nanosheets integrated with telluride nanoparticles: synergistic polysulfide adsorption and catalytic sites for enhanced sulfur redox reactions, *Energy Environ. Sci.* (2025) 1929–1940, <https://doi.org/10.1039/d4ee04689g>.
- [57] C. Huang, J. Yu, C.Yue Zhang, Z. Cui, R. He, L. Yang, B. Niu, C. Li, X. Qi, X. Qi, J. Li, J.Yuan Zhou, O. Usovsev, L. Simonelli, J. Arbiol, Y.J. Lei, Q. Sun, G. Wang, A. Cabot, Anionic doping in layered transition metal chalcogenides for robust lithium-sulfur batteries, *Angew. Chemie - Int. Ed.* (2025), <https://doi.org/10.1002/anie.202420488>.
- [58] C. Li, J. Yu, D. Yang, H. Li, Y. Cheng, Y. Ren, X. Bi, J. Ma, R. Zhao, Y. Zhou, J. Wang, C. Huang, J. Li, I. Pinto-luguet, J. Arbiol, H. Zhang, S. Xin, A. Cabot, Balancing electronic spin State via atomically dispersed heteronuclear Fe – Co pairs for high-performance sodium – sulfur batteries, (2025). [doi:10.1021/jacs.4c15408](https://doi.org/10.1021/jacs.4c15408).
- [59] C.Y. Zhang, J. Yu, C. Huang, G. Sun, J. Li, X. Qi, C.Z. Yi, Metal doping activation of anion mediated electron transfer in catalytic reactions, (2025). [doi:10.1021/jacs.4c18236](https://doi.org/10.1021/jacs.4c18236).
- [60] R. Gancio, R.E. Dumin Borkowski, E. Snoeck, M. Kociak, R. Holmestad, J. Verbeeck, A.I. Kirkland, G. Kothleitner, J. Arbiol, e-DREAM: the European Distributed Research Infrastructure for Advanced Electron Microscopy, *Microsc. Microanal.* 28 (2022) 2900–2902, [doi:10.1017/S1431927622010893](https://doi.org/10.1017/S1431927622010893).

Ligand-Mediated Tailoring of Self-Supported $\text{Mn}_x\text{O}_y\text{@Ni}(\text{OH})_2$ Nanoheterostructures with Enhanced OER Performance

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ABSTRACT: We report a colloidal synthesis strategy for producing $\text{Mn}_x\text{O}_y\text{@Ni}(\text{OH})_2$ nanoheterostructures under mild conditions, i.e., low temperature and ambient pressure. The role of carboxylic acid ligands in directing the synthesis is systematically explored, revealing that lower ligand concentrations along with low-molecular weight molecules favor the formation of well-defined $\text{Mn}_x\text{O}_y\text{@Ni}(\text{OH})_2$ heterostructures. Electrochemical characterization demonstrates that the resulting nanocomposites exhibit significantly enhanced electrochemical surface area and oxygen evolution reaction (OER) activity compared to their single-component counterparts. Specifically, $\text{Mn}_x\text{O}_y\text{@Ni}(\text{OH})_2$ achieves a low overpotential of 299 mV at 10 mA cm^{-2} , a Tafel slope of 61 mV dec^{-1} , and a low charge transfer resistance of 9Ω . The improved OER performance is attributed to the synergistic effect between the $\text{Ni}(\text{OH})_2$ nanosheets, which facilitate $^*\text{OOH}$ intermediate formation, and the MnO_2 component, known for its intrinsic catalytic activity. Additionally, Mn_3O_4 serves as a stabilizing phase and precursor to MnO_2 , contributing to the overall durability and structural integrity of the catalyst.

KEYWORDS: nickel hydroxide, manganese oxide, layer structures, oxides structures, colloidal nanoparticle, oxygen evolution reaction



1. INTRODUCTION

The oxygen evolution reaction (OER) is a key electrochemical process that dictates the efficiency of various renewable energy technologies, including water electrolysis, metal-air batteries, and regenerative fuel cells.^{1–7} However, as a multielectron, kinetically sluggish reaction, OER often represents the rate-limiting step in these systems. To overcome this challenge, efficient catalysts are required to reduce the overpotential and accelerate reaction kinetics. Developing highly active, stable, and cost-effective OER catalysts is essential for advancing sustainable energy conversion and storage technologies.^{8–14}

Noble metals such as Pt and Au, along with metal oxides like RuO_2 and IrO_2 , exhibit excellent catalytic activity and chemical stability for OER.^{15–17} However, their high cost and scarcity have driven research efforts toward more economical and widely available alternatives. Transition metal (TM)-based catalysts, including Mn, Ni, Co, Cu, Zn, and Ti, have emerged as promising alternatives, with optimized formulations achieving electrochemical performances comparable to noble metals.^{18,19}

Among transition metal catalysts, Mn and Ni have attracted significant attention for OER applications. Mn-based oxides are particularly promising for water oxidation, drawing inspiration from the natural OER mechanism in photosystem II

(PSII).^{20,21} In biological systems, OER is facilitated by a Mn_4CaO_5 cluster, stabilized by surrounding amino acid residues, achieving an impressively low OER overpotential (η_{OER}) of 150–300 mV.^{22,23} Synthetic manganese oxides (Mn_3O_4 , MnO_2 , MnO) exhibit reversible redox cycling among Mn^{2+} , Mn^{3+} , and Mn^{4+} oxidation states, making them excellent electronic regulators for enhancing the catalytic performance of other elements, such as Ni.^{24–30}

Similar to Mn, Ni has been identified as a highly active OER catalyst, primarily due to its strong interaction with hydroxyl-adsorbed species and its ideal $\text{Ni}^{3+} [(t_{2g})^6(e_g)^1]$ electronic configuration, which facilitates efficient oxygen-related adsorption and reactivity.^{31,32} This intrinsic reactivity is considered a key factor for designing effective OER catalysts.³³ Notably, the electrochemical performance of Mn_xO_y and $\text{Ni}(\text{OH})_2$ -based

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materials achieves an OER overpotential of around 370 mV at 5 mA cm^{-2} .^{34–40}

Inspired by the potential synergies between Ni- and Mn-based oxides in this study, we developed $\text{Mn}_x\text{O}_y@(\text{Ni}(\text{OH})_2)$ nanoheterostructures using a simple colloidal-based synthesis conducted under low-temperature and ambient conditions. A comprehensive electrochemical evaluation of these nanoheterostructures was performed, with a specific focus on correlating their OER activity with the structure. By carefully optimizing synthetic parameters, such as the type and quantity of carboxylic acid ligands, we achieved a controlled synthesis of self-supported $\text{Mn}_x\text{O}_y@(\text{Ni}(\text{OH})_2)$ nanoheterostructures. This configuration led to notable improvements in the electrochemical performance of $\text{Mn}_x\text{O}_y@(\text{Ni}(\text{OH})_2)$ for OER applications, demonstrating its potential as a cost-effective and scalable catalyst.

2. EXPERIMENTAL SECTION

2.1. Materials. Manganese(II) acetate ($\text{Mn}(\text{Ac})_2$, 98%), nickel(II) acetate ($\text{Ni}(\text{Ac})_2$, 99%), oleylamine (OLA, 98%), oleic acid (OA, 90%), lauric acid (LA, 99%), and xylenes ($\text{C}_6\text{H}_4(\text{CH}_3)_2$, 98.5%) were purchased from Sigma-Aldrich. Potassium hydroxide (KOH, 85%), acetonitrile anhydrous (CH_3CN , 99.8%), and nitric acid (HNO_3 , 70%) were obtained from Thermo Scientific. Tetrafluoroboric acid (HBF_4 , 48% w/w) was purchased from Alfa Aesar. Caprylic acid (CA, 98%) and sulfuric acid (H_2SO_4 , 98%) were purchased from Fluka. Ethanol ($\text{C}_2\text{H}_5\text{OH}$), isopropanol ($\text{C}_3\text{H}_7\text{OH}$), chloroform (CHCl_3), and hexane (C_6H_{14}) were of analytical grade and obtained from Lestlab delivering solutions L.U. Milli-Q water (18 $\text{M}\Omega/\text{cm}$) was supplied by the PURELAB flex from ELGA. All the chemical reagents were used without any additional purification, except for the multiwall carbon nanotubes (MWCNTs).

Carbon cloth (CC) and MWCNT were purchased from Carnd-China. MWCNT underwent purification by being mixed with $\text{HNO}_3/\text{H}_2\text{SO}_4$ (3:1) and subjected to sonication for 1 h. The resulting mixture underwent multiple cycles of precipitation and dispersion using Milli-Q water and ethanol until the supernatant solution reached a pH of approximately 7. Subsequently, they were dried at 60 °C for 24 h.

2.2. Synthesis of Mn_xO_y Nanoparticles. All the experiments were conducted in 50 mL three-neck flasks equipped with a water-cooled condenser and magnetic stirring under room conditions (Figure 1a). 170 mg of $\text{Mn}(\text{Ac})_2$ and 15 mL of xylenes were mixed in a 50 mL three-neck flask and stirred for 10 min. Subsequently, 2.5 mmol of OLA (1 mL) and 2.5 mmol of OA (0.8 mL) were introduced to the mixture. The resulting solution was heated to 100 °C (at a heating rate of 5 °C/min), and then 1 mL of Milli-Q water was injected. The reaction was kept at 100 °C for 3 h. The mixture was allowed to cool down naturally, and then as-synthesized nanoparticles were washed 3 times using isopropanol and chloroform as precipitating and dispersing agents, respectively. It should be noted that this experimental procedure was adapted from previous reports and modified by the inclusion of different ligands and precursors.^{41,42}

To remove the excess organic ligands, the nanoparticles were dispersed in 10 mL of hexane, and then 0.1 mL of HBF_4 dissolved in 10 mL of acetonitrile was added. The nanoparticle solution was sonicated for 10 min and collected through precipitation by adding 10 mL of hexane, followed by centrifugation of the solution at 7500 rpm for 3 min. The supernatant was discarded, and the dark brownish precipitate was redispersed in 5 mL of ethanol. The precipitation–redispersion procedure was repeated three times. Finally, the as-synthesized nanoparticles were dried under an argon flow for 10 min and stored in a sealed vial for further testing.

2.3. Synthesis of $\text{Mn}_3\text{O}_4@(\text{Ni}(\text{OH})_2)$ Nanoheterostructures. The synthesis was carried out by the same procedure described above, but including 120 mg of $\text{Ni}(\text{Ac})_2$ into the initial solution (consisting of $\text{Mn}(\text{Ac})_2$, OLA, OA, and xylenes).

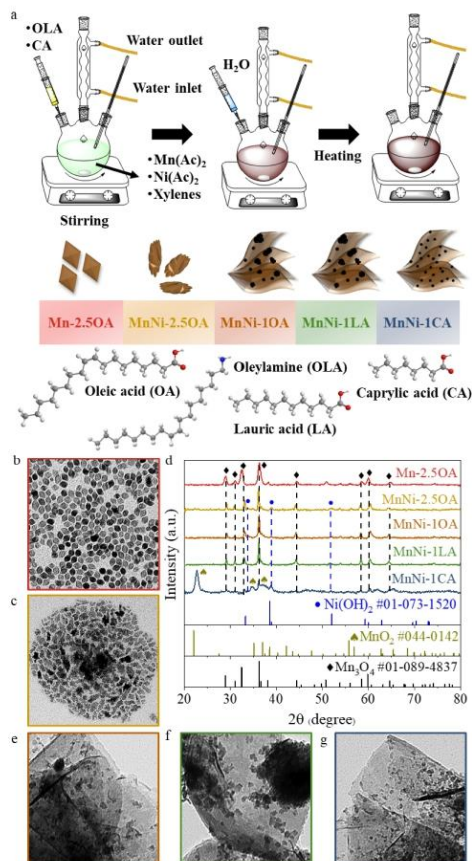


Figure 1. (a) Schematic representation of the experimental procedure used to prepare the different samples, (b) TEM micrograph of Mn_{2.5}OA and (c) MnNi-2.5OA nanoparticles. (d) XRD peaks of Mn_{2.5}OA, MnNi-2.5OA, MnNi-1OA, MnNi-1LA and MnNi-1CA. (e–g) TEM micrographs of (e) MnNi-1OA, (f) MnNi-1LA, and (g) MnNi-1CA.

2.4. Synthesis of $\text{Mn}_x\text{O}_y@(\text{Ni}(\text{OH})_2)$ Nanoheterostructures. To synthesize the $\text{Mn}_x\text{O}_y@(\text{Ni}(\text{OH})_2)$ nanoheterostructures, the amount of OA was reduced from 2.5 to 1 mmol keeping the other conditions constant (method detailed above). Additionally, OA was substituted with either LA or CA while maintaining the same amount (i.e., 1 mmol).

2.5. Structural and Chemical Characterization. The samples were characterized through transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) using a Tecnai F20, operating at 200 kV with a point-to-point resolution of 0.19 nm. Sample preparation involved drop-casting diluted solutions of nanoparticles onto a carbon-coated copper grid (200 mesh, TED PELLA, INC.). Images were analyzed using Gatan Digital Micrograph software. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was combined with electron energy loss spectroscopy (EELS) in the Tecnai F20 by using a Gatan Quantum energy filter. Images and elemental mapping were measured in a spherical aberration-corrected transmission electron microscope FEI Titan G2

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80–200 Chemi STEM with four energy-dispersive X-ray spectroscopy (EDX) detectors, operated at 80 and 200 keV. The crystalline structure of the samples was analyzed by X-ray diffraction (XRD) patterns obtained from a Bruker AXS D8 Advance X-ray diffractometer with Ni-filtered ($2\ \mu\text{m}$ thickness) $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406\ \text{\AA}$) operated at 40 mA and 40 kV. Scanning electron microscopy (SEM) images were obtained using a ZEISS Auriga microscope equipped with an energy-dispersive X-ray spectroscopy (EDS) detector operating at 20 kV. The samples were prepared by dispersing the nanoparticles in ethanol, and the dilute solution was drop-casted onto silicon substrates placed on aluminum specimen mount with carbon tape. The elements' chemical states were analyzed by X-ray photoelectron spectroscopy (XPS) on a SPECS system equipped with an Al anode XPS source operating at 150 W and a Phoibos 150 MCD-9 detector. The pressure in the analysis chamber was always below 10^{-7} Pa. The area analyzed was about $2 \times 2\ \text{mm}$. The pass energy of the hemispherical analyzer was set to 25 eV, and the energy step was set to 0.1 eV. Data processing was performed with the Multipak data reduction software (Physical Electronic-PHI, Inc., EE. UU.). Binding energy (BE) values were corrected using the C 1s peak at 284.8 eV. Inductively coupled plasma optical emission spectrometry (ICP-OES) was performed using Shimadzu ICPE-9820 simultaneous ICP atomic emission spectrometers.

2.6. Electrochemical Characterization. All electrochemical measurements were conducted at room temperature using a model CHI760E electrochemical workstation (Shanghai Chenhua Instrument Co. Ltd., China) within a standard three-electrode cell. A platinum mesh served as the counter electrode, while a Hg/HgO electrode was utilized as a reference. The reference electrode potential was converted to RHE using the provided equation (eq 1).^{43,44}

$$E_{\text{RHE}} = E_{\text{applied}} + E_{\text{Hg/HgO}} + (0.059 \times \text{pH}) \quad (1)$$

For the working electrode preparation, a 250 μL ink solution was aerosol-deposited onto both sides of a CC ($14 \times 10\ \text{mm}$), supported on a heating plate at $60\ ^\circ\text{C}$. The ink solution was prepared by dispersing 3 mg of nanoparticles and 1 mg of MWCNT in 750 μL of isopropanol. Subsequently, 220 μL of Milli-Q water and 30 μL of 5 wt % Nafion were added to the mixture. The resulting solution was sonicated for 1 h to ensure homogeneity. Electrochemical tests were carried out using 1 M of KOH solution ($\text{pH} = 13.8$) as the electrolyte. Linear sweep voltammetry (LSV) measurements were performed in 1 M KOH with a scan rate of 5 mV/s covering a potential range from 1 to 1.6 V vs RHE in the anodic direction. Tafel slopes were extracted from LSV curves by transforming the current axes into logarithm and potential axes into overpotential, considering a range potential of $\pm 20\ \text{mV}$ around η_{OER} . Electrochemical impedance spectroscopy (EIS) tests were recorded using the overpotential value obtained from LSV. The frequency window was set from 10^5 to 0.1 Hz, and a potential amplitude of 5 mV was employed.

Cyclic voltammetry (CV) was performed at various scan rates (10, 20, 40, 60, 80, 100 mV/s) with a $\pm 50\ \text{mV}$ range centered around the open circuit potential (OCP, nonfaradaic region). The electrochemical double-layer capacitance (C_{dl}) was calculated from the CV data by plotting a graph of the subtraction of anodic and cathodic charge currents (Δi , eq 2) against scan rate (ν). This plot exhibited a linear correlation, and the slope of this line corresponds to the C_{dl} , as described by eq 3.⁴⁴

$$\Delta i(A) = \left(\frac{i_{\text{anodic}} + i_{\text{cathodic}}}{2} \right)_{\text{OCP}} \quad (2)$$

$$\text{Slope} = C_{\text{dl}}(F) = \frac{\Delta i(A)}{\nu(\text{V/s})} \quad (3)$$

The electrochemical surface area (ECSA, eq 4) was calculated using the specific charge density (C_s) reported for a 1 M of NaOH solution (40 $\mu\text{F}/\text{cm}^2$).^{44,45}

$$\text{ECSA}(\text{cm}^2) = C_{\text{dl}}(\mu\text{F}) / C_s(\mu\text{F cm}^{-2}) \quad (4)$$

Surface coverage (Γ^*) and diffusion coefficient (D) parameters of the $\text{Ni}(\text{OH})_2/\text{NiOOH}$ redox species were determined from CV curves recorded at different scan rates using eqs 5 and 6, respectively.

$$i_p = \left(\frac{n^2 F^2}{4RT} \right) A \Gamma^* \nu \quad (5)$$

$$i_p = 2.69 \times 10^5 n^{3/2} D^{1/2} \nu^{1/2} C_A \quad (6)$$

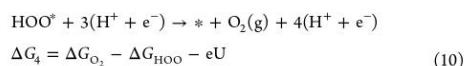
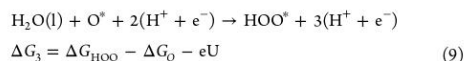
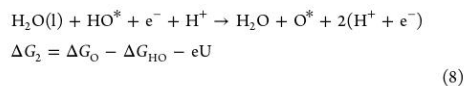
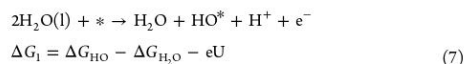
Here, i_p represents the average current at the redox peaks in the CV curve, A is the geometric surface area of the electrode ($1\ \text{cm}^2$), n is the number of electrons transferred (assumed to be 1 for the $\text{Ni}(\text{OH})_2/\text{NiOOH}$ redox process), F is the Faraday constant ($96,485\ \text{C mol}^{-1}$), R is the gas constant ($8.314\ \text{J K}^{-1}\ \text{mol}^{-1}$), and T is the absolute temperature ($298\ \text{K}$).⁴⁶

The stability of the MnNi-1CA electrode was evaluated by chronoamperometry in 1.0 M KOH solution at room temperature. A constant potential of 1.6 V vs RHE, corresponding to the onset potential for oxygen evolution, was applied, and the current response was monitored over 24 h. Additionally, a second chronoamperometric test was performed at 1.7 V vs RHE, a value chosen above the overpotential associated with OER activity, to assess the material's performance under more demanding electrochemical conditions.

2.7. Computational Method. Spin-polarized density functional theory (DFT) calculations were performed using the Vienna ab initio Simulation Package (VASP) with the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) exchange–correlation functional.⁴⁷ The core electrons were treated with projector augmented wave (PAW) pseudopotentials.⁴⁸ The Hubbard U approach (DFT + U) was adopted to describe the Coulomb correlation for Ni with $U-J = 5.5\ \text{eV}$, and for Mn with $U-J = 3.9\ \text{eV}$.^{49,50} A cutoff energy of 520 eV was used for the plane-wave basis set, and a threshold of self-consistent-field energy convergence was $1 \times 10^{-5}\ \text{eV/atom}$. The convergence criterion for the structural optimizations was a maximum force of 0.03 eV/ $\text{\AA}$. The k-point meshes were $3 \times 3 \times 1$ with the Monkhorst–Pack method since the supercell is large enough.⁵¹

Mn_3O_4 supported NiOOH was constructed to represent the NiOOH/ Mn_3O_4 composite, while a heterostructure consisting of Mn_3O_4 and MnO_2 with oxygen vacancies supported on NiOOH was used to describe the NiOOH/ Mn_3O_4 – MnO_2 catalyst. A vacuum layer of 15 $\text{\AA}$ thickness was used in the z-direction to eliminate the interaction between the surfaces in the slab models.

During the structure optimization, the two bottom atomic layers of manganese oxide were fixed, and all other atoms were fully relaxed. The OER consists of four elementary reaction steps, and the computational hydrogen electrode (CHE) model proposed by Nørskov was used to calculate the Gibbs free energy according to the following equations:⁵²



ΔG_1 , ΔG_2 , ΔG_3 , and ΔG_4 are the free energy changes of the four reaction steps in OER. The symbol * means the clean catalysts. HO^* , O^* , and HOO^* represent the adsorbed intermediates HO, O, and HOO on the catalysts, respectively.

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$$\Delta G = \Delta E + \Delta ZPE - T\Delta S + \Delta G_U + \Delta G_{\text{pH}} \quad (11)$$

ΔE represents the adsorption energy of various adsorbed intermediates obtained from DFT calculations. ΔZPE is the change of zero-point energy, T is the temperature, ΔS is the difference in entropy, and the entropy energy contributions were neglected here. When $\text{pH} = 0$, $T = 298 \text{ K}$, $p = 1 \text{ bar}$, and the electrode potential (U) was zero, the chemical potential for ($\text{H}^+ + \text{e}^-$) was equal to that of $1/2 \text{ H}_2$ gas phase. In addition, $\Delta G_U = -eU$, where U was the potential of the electrode relative to the standard hydrogen electrode. In this work, the calculation condition was set to $\text{pH} = 0$; thus, the correction value ΔG_{pH} can be ignored. Moreover, the overpotential η of the electrocatalyst was determined by eq 6:

$$\eta = \max\{\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4\}/e - 1.23 \text{ V} \quad (12)$$

3. RESULTS AND DISCUSSION

3.1. Structural and Chemical Characterization. Mn_xO_y was synthesized through the decomposition of manganese acetate (MnAc_2) in the presence of OLA, OA, and water in xylene at 100°C under atmospheric conditions. The samples were labeled as Mn-2.SOA (manganese precursor with 2.5 mmol OA) and MnNi-2.SOA (same as Mn-2.SOA but with added nickel precursor). MnNi-1.OA, MnNi-1.LA, and MnNi-1.CA were synthesized with both manganese and nickel precursors, where the carboxylic acid quantity was reduced to 1 mmol using OA, LA, and CA, respectively. TEM in Figure 1b reveals that the synthesized Mn_xO_y particles exhibit a bipyramidal morphology. XRD analysis further confirms that the Mn_xO_y particles primarily crystallize in the Mn_3O_4 hausmannite phase (Figure 1d).

When a 50% molar mass (Ni vs Mn) of nickel acetate (NiAc_2) was added to the reaction flask, irregularly shaped particles were obtained (Figure 1c). In addition to the Mn_3O_4 hausmannite phase, XRD patterns revealed diffraction peaks corresponding to the (100), (002), and (012) crystallographic planes of $\text{Ni}(\text{OH})_2$ (Figure 1d, yellow line).

To assess the impact of OA on the growth of $\text{Mn}_x\text{O}_y/\text{Ni}(\text{OH})_2$, both its concentration and carbon chain length were systematically varied. Reducing the OA concentration from 2.5 to 1 mmol resulted in the formation of $\text{Mn}_x\text{O}_y/\text{Ni}(\text{OH})_2$ self-supported nanoheterostructures, where nanoparticles are supported on a nanosheet (Figure 1e). A similar morphology was observed when OA was replaced with 1 mmol of LA and CA (Figure 1f,g). Among these, the CA-derived sample exhibited the most homogeneous particle dispersion with minimal aggregation, suggesting a better stabilization effect.

XRD analysis confirmed that samples synthesized using OA and LA primarily contained Mn_3O_4 hausmannite and $\text{Ni}(\text{OH})_2$ phases (Figure 1d). In contrast, the sample obtained with CA exhibited additional diffraction peaks corresponding to the (101), (301), and (210) crystallographic planes of the ramsdellite MnO_2 phase (Figure 1d), indicating a distinct structural evolution influenced by the carboxylic acid ligand.

The Mn and Ni content was quantified using ICP-OES analysis, with the results presented in Table S1. Overall, the Mn/Ni ratio remained consistent across all samples, closely matching the nominal values of the precursor materials, indicating reliable compositional control during synthesis.

The structural and compositional analysis of the synthesized nanocomposites, demonstrated by HRTEM images and HAADF-STEM with EELS, provides valuable insights into the phase evolution and morphology of the samples. Figure 2 presents a detailed structural and compositional analysis of

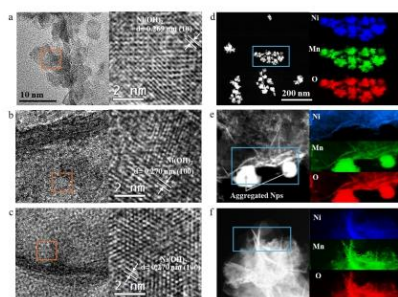


Figure 2. (a–c) HRTEM micrographs with magnified lattice fringe visualized in the orange square and (d–f) HAADF STEM general views of the nanostructures together with selected area STEM-EELS composition maps of the MnNi-2.SOA, MnNi-1.OA, and MnNi-1.CA samples.

$\text{Mn}_x\text{O}_y/\text{Ni}(\text{OH})_2$ self-supported nanoheterostructures synthesized with varying concentrations and chain lengths of carboxylic acids, specifically focusing on MnNi-2.SOA, MnNi-1.OA, and MnNi-1.CA samples. HRTEM images (Figure 2a–c) reveal clear lattice fringes for all three samples, with an interplanar spacing of $\sim 0.269\text{--}0.270 \text{ nm}$ indexed to the (100) planes of $\text{Ni}(\text{OH})_2$. These fringes confirm the crystalline nature of the $\text{Ni}(\text{OH})_2$ component across all samples.

The MnNi-2.SOA sample (Figure 2a) synthesized with a higher OA concentration demonstrates well-defined and continuous lattice fringes, indicative of high crystallinity and structural integrity. In contrast, reducing the OA concentration to 1 mmol (MnNi-1.OA, Figure 2b) results in more disordered nanosheet structures with embedded Mn_xO_y -supported nanoparticles. The lattice fringes remain visible but slightly less distinct, suggesting a moderate impact on crystalline ordering.^{53–55} Interestingly, the MnNi-1.CA sample (Figure 2c), derived using 1 mmol of CA—a shorter-chain fatty acid—exhibits similarly ordered fringes but with improved overall homogeneity and minimal visible aggregation.

The STEM-EELS mapping (Figure 2d–f) further underscores the influence of surfactant identity on elemental distribution. In the MnNi-2.SOA sample, Ni, Mn, and O are uniformly distributed, corresponding to well-stabilized and discrete nanoparticle assemblies. In contrast, the MnNi-1.OA sample shows clear nanoparticle aggregation, evident from the white contrast regions in the HAADF-STEM image and overlapping Ni and Mn signals. This is attributed to the lower OA concentration, which reduces steric stabilization during synthesis. Interestingly, the MnNi-1.CA sample exhibits a highly uniform elemental distribution with no obvious aggregation, despite CA's shorter alkyl chain. This improved stabilization is likely due to CA's combination of steric and electrostatic effects, which enhance particle dispersion at lower concentrations.^{56–58} In summary, these results highlight how both the concentration and molecular structure of carboxylic acid surfactants critically influence the crystallinity, elemental distribution, and aggregation behavior of the $\text{Mn}_x\text{O}_y/\text{Ni}(\text{OH})_2$ nanoheterostructures. Lower OA concentrations lead to aggregation, while CA enables uniform particle dispersion even at reduced surfactant levels, demonstrating a clear correlation between synthesis conditions, structure, and composition.

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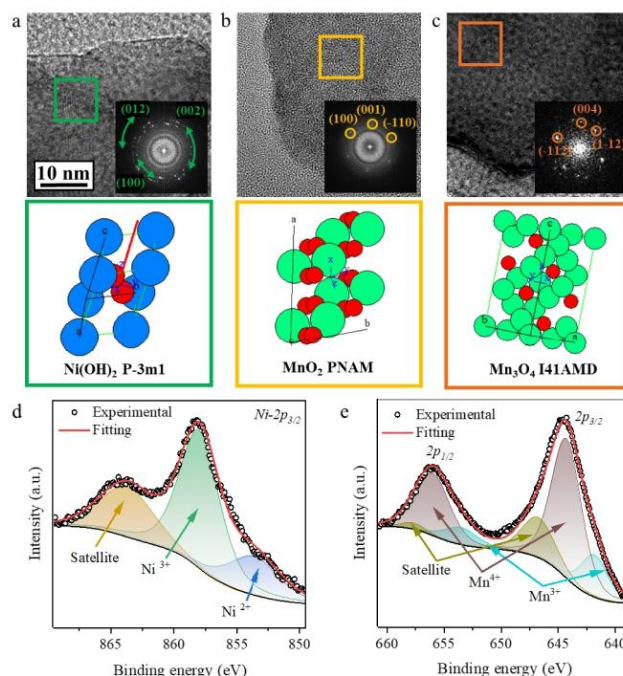


Figure 3. (a–c) HRTEM micrographs, corresponding fast Fourier transformation (FFT) patterns (inset), and crystallographic structure models identified in each region of the MnNi-1CA sample. (d, e) High-resolution Ni $2p_{3/2}$ and Mn $2p$ XPS spectra of MnNi-1CA.

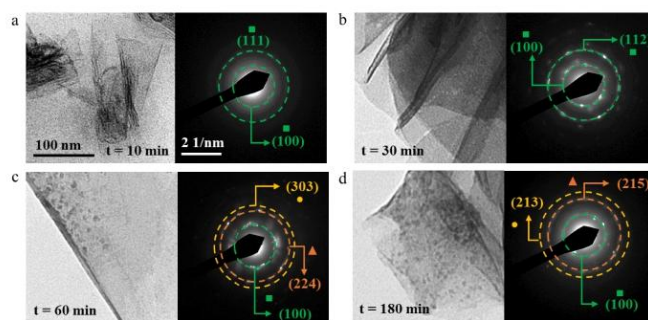


Figure 4. TEM micrograph and corresponding SAED pattern evolution of MnNi-1CA at different synthesis times: (a) $t = 10$ min, (b) 30 min, (c) 60 min, and (d) 180 min after water injection. The diffraction rings highlighted in green (■) correspond to the crystal structure of $\text{Ni}(\text{OH})_2$, while those in yellow (●) and orange (▲) are associated with the crystal structures of MnO_2 and Mn_3O_4 , respectively.

Figure 3 displays additional HRTEM images of the $\text{Mn}_x\text{O}_y/\text{Ni}(\text{OH})_2$ nanoheterostructures obtained with CA. The nanosheet exhibits the crystal structure of $\text{Ni}(\text{OH})_2$ (Figure 3a), while the nanoparticles show the MnO_2 and Mn_3O_4 phases (Figure 3b and 3c). The Ni $2p_{3/2}$ XPS spectrum of $\text{Mn}_x\text{O}_y/\text{Ni}(\text{OH})_2$ obtained with CA was deconvoluted into three peaks associated with Ni^{2+} in $\text{Ni}(\text{OH})_2$ at 853.6 eV, Ni^{3+} in NiOOH at 858.1 eV, and a satellite peak (Figure 3d). The Mn $2p$ XPS spectrum displays two doublets corresponding to Mn^{3+} and Mn^{4+} oxidation states (Figure 3e). These species, identified in

the XPS spectra, are consistent with the Mn_3O_4 and MnO_2 phases observed in the HRTEM images, supporting the coexistence of both phases in the nanoheterostructures.

The TEM micrographs and corresponding selected area electron diffraction (SAED) patterns of MnNi-1CA at different synthesis times reveal a time-dependent crystallization mechanism (Figure 4). After the addition of water, thin, sheet-like structures corresponding to $\text{Ni}(\text{OH})_2$ begin to nucleate after 10 min of reaction, as confirmed by the diffraction rings of the (100) and (111) planes (Figure 4a).

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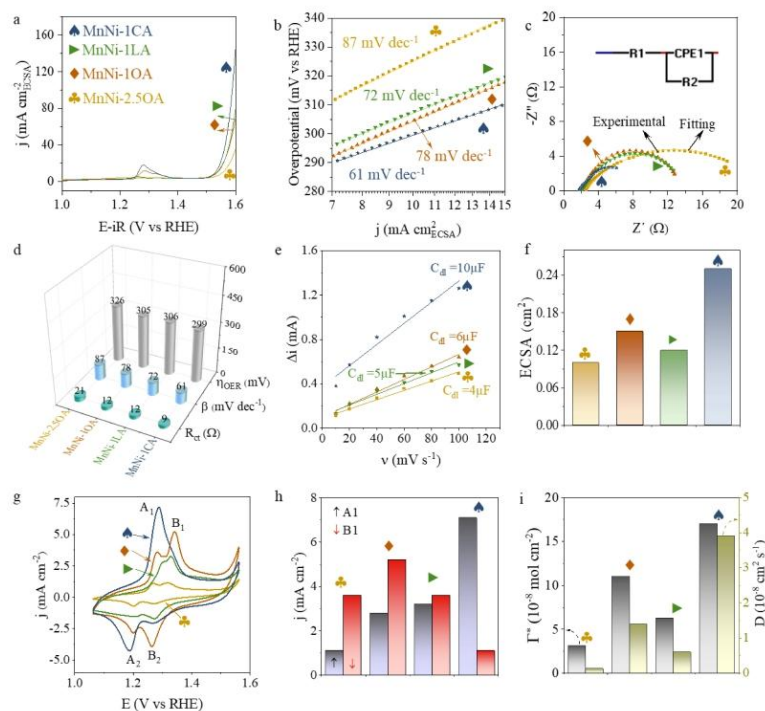


Figure 5. Electrochemical performance in 1 M KOH solution: (a) LSV curves at 5 mV/s, (b) Tafel plots, with the β extracted from the LVS curve at $\eta_{\text{OER}} \pm 20$ mV, and (c) Nyquist plots measured at η_{OER} and equivalent circuit used to fit the data (see Table S2). (d) Comparison of η_{OER} , β , and R_{ct} . (e) Determination of C_{dl} from the slope of the linear fit of Δi vs v and (f) ECSA. (g) CV curve at 10 mV s⁻¹ and (h) peak current densities extracted from CV curves at 10 mV s⁻¹, corresponding to the oxidation of Ni(OH)₂ (A₁) and Mn₂O₃ (B₁). (i) Comparison of Γ^* and D of redox species for MnNi-2.5OA, MnNi-1OA, MnNi-1LA, and MnNi-1CA.

Water plays a critical role in the nucleation and growth of Ni(OH)₂, facilitating the hydrolysis and precipitation processes.⁷ As the reaction progresses, these nanosheets grow larger and more defined, with the appearance of the (112) plane indicating increased crystallinity and structural organization ($t = 30$ min, Figure 4b). By 60 min, the TEM image shows denser nanosheets with small nanocrystals forming on the surface, marking the transition from a pure hydroxide phase to a mixed-phase system, which is further validated by new SAED diffraction rings corresponding to MnO₂ (303) and Mn₃O₄ (224), suggesting the progressive incorporation of Mn species. Finally, at 180 min, the morphology becomes more compact and granular, indicating the final stabilization of mixed metal oxides, with the SAED pattern exhibiting stronger MnO₂ and Mn₃O₄ reflections, including the (213) and (215) planes. This demonstrates the complete structural transformation from hydroxides to a stable mixed-metal oxide phase driven by prolonged reaction time, crystallization processes, and the presence of water.

In addition to the critical role of water, the concentration of carboxylic acid ligands also significantly influences the crystallization pathway and final morphology. Experimental results using OA, LA, and CA consistently show that lower ligand concentrations favor the formation of thin, two-

dimensional heterostructures, whereas higher concentrations tend to stabilize smaller, more isotropic nanoparticles. This behavior is attributed to the dynamic competition between ligand adsorption and precursor nucleation: at low concentrations, partial surface coverage by carboxylate groups facilitates lateral growth of Ni(OH)₂ nanosheets and the subsequent anchoring of Mn-based nanocrystals.

DFT calculations using OA as a model ligand support this interpretation. The results reveal preferential adsorption on the Mn₃O₄-MnO₂ region (-1.32 eV) of the Ni(OH)₂/Mn₃O₄-MnO₂ heterostructure, compared to weaker adsorption on the Ni(OH)₂ region (-0.94 eV), as shown in Figure S5. This disparity suggests that ligand binding helps stabilize specific regions of the heterostructure, promoting anisotropic growth and interface formation. The adsorption occurs primarily via O and OH coordination from the carboxylic headgroup, a mode likely shared across all three acids studied. These findings indicate that ligand concentration is the dominant factor in directing 2D heterostructure assembly, with molecular identity playing a secondary role due to the shared binding motif of carboxylic acids. However, the molecular structure of the ligand becomes increasingly important in determining crystallinity, elemental distribution, and aggregation behavior,

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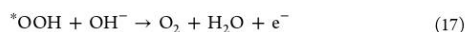
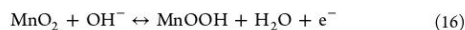
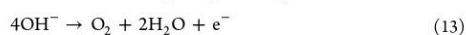
as observed in the different outcomes for OA, LA, and CA at comparable concentrations.

3.2. Electrochemical Characterization. Electrodes were prepared by spray coating CC with a solution containing $\text{Mn}_3\text{O}_4/\text{Ni}(\text{OH})_2$ and MWCNT. The combination of CC providing a conductive support, while MWCNTs promote the dispersion of active materials, results in efficient charge transfer, enhanced material distribution, and improved electrochemical performance. SEM-EDS analysis (Figures S1–S4) revealed a homogeneous coverage of the CC fibers. The LSV data have been iR -corrected and normalized to the ECSA to allow for accurate comparison of intrinsic activity.^{59–62} Figure 5a shows the curves in an alkaline electrolyte obtained for the different electrodes.¹⁷ MnNi-1CA exhibited the lowest η_{OER} (299 mV at 10 mA cm^{-2}) involving improved thermodynamics and the lowest Tafel slope ($\beta = 61 \text{ mV dec}^{-1}$, Figure 5b), indicating superior OER kinetics.

Electrochemical impedance spectroscopy (EIS) was conducted to determine the charge transfer resistance of each sample under kinetic control during the OER process. The experimental data were fitted using an equivalent circuit consisting of a resistance (R_1) in series with a resistive/capacitive element ($R_2/\text{CPE1}$), where R_1 represents the solution resistance, CPE1 accounts for the pseudocapacitance of the double layer, and R_2 corresponds to the charge transfer resistance (R_{ct}). MnNi-1CA exhibited the smallest semicircle in the Nyquist plot, indicating the lowest R_{ct} value (9Ω), as shown in Figure 5c. In addition, Figure 5d and Table S2 illustrate the correlation between η_{OER} , β , and R_{ct} across the different samples. These results suggest that lower charge transfer resistance is associated with enhanced OER kinetics and improved electrocatalytic activity. In particular, the superior performance of MnNi-1CA can be attributed to its more efficient charge transfer at the electrode–electrolyte interface, which facilitates faster reaction kinetics during the OER process.

The ECSA was determined by analyzing the double-layer capacitance (C_{dl}), acquired through CV at varying scan rates (Figures 5e and 5f). Consistent with previous results, MnNi-1CA also demonstrated the highest ECSA value, at 0.25 cm^2 (Figure 5f and Table S3).

Figure 5g presents CV plots at 10 mV s^{-1} for MnNi-2.SOA, MnNi-1OA, MnNi-1LA, and MnNi-1CA electrodes. In this figure, peak A_1 corresponds to the oxidation process of $\text{Ni}(\text{OH})_2$, while A_2 represents the subsequent reduction of NiOOH. Peaks B_1 and B_2 reflect the overlapping oxidation and reduction processes of MnO_2 and Mn_3O_4 . The peak current densities A_1/A_2 observed at lower potentials (~ 1.2 – 1.3 V vs RHE) are consistent with the redox activity of Ni-based species (eq 14). In contrast, the B_1/B_2 peaks, occurring at slightly higher potentials (~ 1.3 – 1.4 V vs RHE), correspond to Mn-based redox reactions, including the formation of higher oxidation states such as MnOOH (eqs 15 and 16).^{63–65} The generation of oxyhydroxide species ($^*\text{OOH}$) during these oxidation processes is essential for creating active sites that significantly enhance the overall OER (eq 17). As demonstrated in eqs 13–17, the oxidation of $\text{Ni}(\text{OH})_2$, MnO_2 , and Mn_3O_4 leads to the formation of $^*\text{OOH}$ species, which play a critical role in initiating and promoting the OER.^{45,66–68}



Among the tested samples, MnNi-1CA exhibited the highest peak current density at A_1 (Figure 5h), indicating the most efficient redox activity of the $\text{Ni}(\text{OH})_2/\text{NiOOH}$ couple. In contrast, the other samples demonstrated greater activity for the Mn_3O_4 and MnO_2 redox reaction (B_1), as evidenced by their higher current density peak values compared to that of the $\text{Ni}(\text{OH})_2/\text{NiOOH}$ redox peaks, but showed intrinsically lower activity than the $\text{Ni}(\text{OH})_2/\text{NiOOH}$ couple in the context of the OER. This observation suggests that MnNi-1CA possesses a greater number of electrochemically active sites and enhanced charge transfer kinetics. Importantly, the overlapping redox processes of Ni and Mn species create a dynamic interfacial environment where simultaneous oxidation and reduction reactions facilitate efficient electron transfer and stabilize critical $^*\text{OOH}$ intermediates. This synergistic overlap enhances the overall OER performance by optimizing the availability and activity of catalytic sites on the electrode surface.

The superior performance of MnNi-1CA is attributed to the unique composition, where the $\text{Ni}(\text{OH})_2$ nanosheet supports both Mn_3O_4 and MnO_2 nanoparticles, in contrast to the other samples, which only feature Mn_3O_4 nanoparticles on $\text{Ni}(\text{OH})_2$ nanosheets. The presence of MnO_2 in MnNi-1CA plays a crucial role in boosting catalytic performance, as it is more active for OER compared to Mn_3O_4 . Although Mn_3O_4 is less active for OER, it serves as both a precursor to MnO_2 under OER conditions and as a stabilizing phase.⁶⁹ Furthermore, the proton diffusion barrier, often a rate-limiting factor in the $\text{Ni}(\text{OH})_2/\text{NiOOH}$ transition, is effectively reduced in MnNi-1CA.⁷⁰ This is demonstrated by its highest surface coverage (Γ^*) and diffusion coefficient (D , Figures 5i, 5j, and 5k).

Complementary XPS analysis (Figure S9, Table S4) further supports this behavior, showing that the Ni species remain in a stable NiOOH-like state after CV cycling, while Mn species undergo redox evolution ($\text{Mn}^{4+} \rightarrow \text{Mn}^{3+}/\text{Mn}^{2+}$). This indicates that Mn_3O_4 serves as a redox-active yet structurally stable support, promoting the activity of the NiOOH phase through dynamic surface interactions.

When comparing the performance of sample MnNi-1CA (299 mV at 10 mA cm^{-2}) with current state-of-the-art catalysts, a significant improvement in the overpotential is observed (Table S5). For instance, the overpotential is clearly lower than those reported for $\text{Ni}(\text{OH})_2$, MnO_2 , and Mn_3O_4 (391, 381, and 370 mV, respectively),^{34,40,71} and even compared to nanoheterostructures containing MnO_2 combined with Ni or $\text{Ni}(\text{OH})_2$ (580, 474, 410, and 400 mV, respectively).^{36–39} Notably, the overpotential of MnNi-1CA also outperforms that of the benchmark OER electrocatalyst RuO_2 (360 mV).³⁵ Our results are only surpassed by recently developed atomically dispersed Gd- MnO_2 nanoparticles and comparable to Gd@ MnO_2 nanoheterostructures (281 and 323 mV, respectively).⁷¹ This enhanced electrocatalytic performance can be attributed to the synergistic interaction between Mn and Ni domains, as well as the formation of heterojunctions within the nanoheterostructures—specifically between MnO_2 – Mn_3O_4 and these manganese oxides with the $\text{Ni}(\text{OH})_2$ nanosheet.

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The stability of the MnNi-1CA sample was assessed through chronoamperometry at two different potentials. At a fixed potential of 1.7 V vs RHE, which is above the OER overpotential, the current rapidly decreased within the first few hours, indicating significant electrode degradation under these harsher conditions (Figure S10a). In contrast, at a lower potential of 1.6 V vs RHE, close to the onset potential, the material exhibited stable performance for about 24 h. This suggests that MnNi-1CA is more durable under milder conditions, maintaining its activity over a longer duration without significant degradation. Moreover, LSV measurements taken before and after chronoamperometry at 1.6 V vs RHE (Figure S10b) showed no significant change in current density across the tested potential window, further confirming that the material does not undergo noticeable degradation under these conditions. This stability at 1.6 V contrasts with its instability at higher potential values, indicating that MnNi-1CA is stable under milder operational conditions, but further optimization is required to improve its performance and stability at higher potential values for prolonged use.

In addition to experimental investigations, DFT calculations were performed to gain a fundamental understanding of the effect of single Mn_3O_4 and $\text{Mn}_3\text{O}_4\text{-MnO}_2$ heterostructures on the NiOOH OER performance. Considering only the four-electron ($4e^-$) reaction pathway shown in eqs 7–10, the Gibbs free energy of each elementary step for the adsorbate evolution mechanism (AEM) either on the surface of NiOOH/ Mn_3O_4 or NiOOH/ $\text{Mn}_3\text{O}_4\text{-MnO}_2$ was calculated, respectively. The calculated adsorption structures are shown in Figures S11–S13. According to the calculations for the Gibbs free energy, the reaction of step II, from $^*\text{OH}$ to $^*\text{O}$, is the rate-determining step for both NiOOH/ Mn_3O_4 (2.12 eV) and NiOOH/ $\text{Mn}_3\text{O}_4\text{-MnO}_2$ (1.92 eV) with the overpotential of 0.89 and 0.69 V, respectively (Figure 6a). Furthermore, the overpotential for the lattice oxygen oxidation mechanism (LOM) proceeded on the interface of NiOOH/ $\text{Mn}_3\text{O}_4\text{-MnO}_2$ is only 0.57 V. In this case, the largest Gibbs free energy change is 0.12 eV smaller than that for AEM on the surface of NiOOH/ $\text{Mn}_3\text{O}_4\text{-MnO}_2$. Thus, the LOM mechanism requires a lower overpotential to drive the oxidation of water. Overall, our calculations show that the OER catalytic activity of NiOOH/ $\text{Mn}_3\text{O}_4\text{-MnO}_2$ can be significantly increased by introducing $\text{Mn}_3\text{O}_4\text{-MnO}_2$ heterostructure composite and that the LOM mechanism is more favorable, which is consistent with the experimental results. Furthermore, charge density differences were further analyzed comparatively for NiOOH/ Mn_3O_4 and NiOOH/ $\text{Mn}_3\text{O}_4\text{-MnO}_2$. As shown in Figure 6, when the $\text{Mn}_3\text{O}_4\text{-MnO}_2$ heterostructure serves as the support for NiOOH, more electrons transfer to the NiOOH and accumulate especially at the interface of NiOOH/ $\text{Mn}_3\text{O}_4\text{-MnO}_2$, leading to convenient electron transfer from the catalysts to the oxygen species, which facilitates the OER through the electron modulation.

4. CONCLUSION

$\text{Mn}_x\text{O}_y\text{@Ni(OH)}_2$ was successfully synthesized using a low-temperature colloidal method. Notably, a reduction in carboxylic acid content from 2.5 to 1 mmol resulted in the formation of Ni(OH)_2 nanosheets. This structural alteration proved pivotal in enhancing the electrochemical properties of the investigated materials for OER. Among the materials tested, MnNi-1CA exhibited the most promising outcomes, displaying a remarkably low overpotential of 299 mV at 10 mA

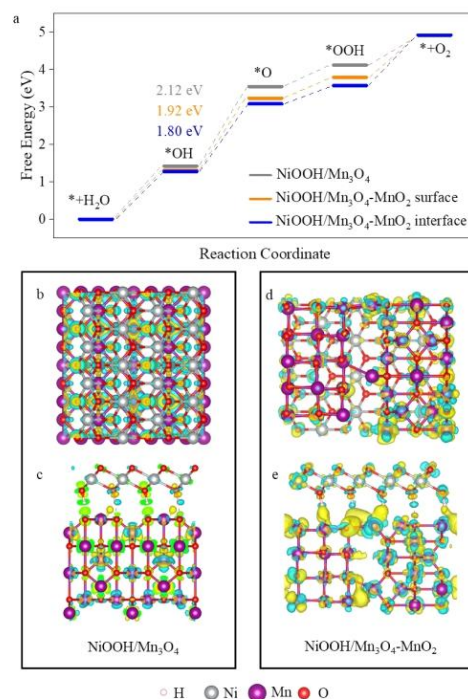


Figure 6. (a) Free energies of OER steps on the surface of NiOOH/ Mn_3O_4 and surface/interface of NiOOH/ $\text{Mn}_3\text{O}_4\text{-MnO}_2$. (b–e) Charge density difference of (b) top-view and (c) side-view of NiOOH/ Mn_3O_4 , (d) top-view and (e) side-view of NiOOH/ $\text{Mn}_3\text{O}_4\text{-MnO}_2$. The isosurface is $0.002 \text{ e}\text{\AA}^{-3}$.

cm^{-2} . This advantageous performance can be associated with its minimal Tafel slope (61 mV dec^{-1}), low R_{ct} value (9Ω), and substantial surface-active area (0.53 cm^2). These favorable characteristics can be attributed to the presence of a MnO_2 phase and the formation of a $\text{Mn}_3\text{O}_4\text{-MnO}_2$ heterostructure (heterojunction). Synergistic interactions among NiOOH/ $\text{Mn}_3\text{O}_4\text{-MnO}_2$ nanoheterostructures result in a catalytic environment that enhances charge transfer and stabilizes key oxygen evolution intermediates ($^*\text{OH}$, $^*\text{O}$, and $^*\text{OOH}$). Moreover, DFT calculation along with experimental results points toward a LOM as the dominant OER mechanism delivering overpotential as low as 299 mV. Overall, this study provides new insights into the synthesis of $\text{Mn}_x\text{O}_y\text{@Ni(OH)}_2$ nanoheterostructures via the modulation of different ligands. This approach not only involves their evolution from 0D to a 2D arrangement but also highlights their enhanced electrochemical properties.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.5c07315>.

SEM images and EDS spectra of $\text{Mn}_x\text{O}_y\text{@Ni(OH)}_2$ electrodes; DFT-calculated adsorption energies on

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NiOOH, Mn_2O_4 , and NiOOH/ Mn_2O_4 - MnO_2 surfaces; CV curves and scan rate-dependent behavior; analysis of diffusion and kinetic parameters; post-CV XPS spectra of Mn and Ni; chronoamperometric stability tests and LSV curves before/after operation; optimized structures of OER intermediates (*OH, *O, *OOH) under AEM and LOM pathways; ICP-OES analysis of Mn/Ni ratios; thermodynamic, kinetic, and electrochemical parameters for OER; XPS quantification of surface states pre- and postcycling; benchmarking of overpotential performance versus literature (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Baek, W.; Chang, H.; Bootharaju, M. S.; Kim, J. H.; Park, S.; Hyeon, T. Recent Advances and Prospects in Colloidal Nanomaterials. *JACS Au* **2021**, *1* (11), 1849–1859.
- (2) Cai, Z.; Chen, X.; Yao, Q.; Wang, X. Nanomaterials With Different Dimensions for Electrocatalysis. In *Novel Nanomaterials for Biomedical, Environmental and Energy Applications*; Elsevier: 2019, pp. 435–464.
- (3) Lu, Z.; Yin, Y. Colloidal Nanoparticle Clusters: Functional Materials by Design. *Chem. Soc. Rev.* **2012**, *41* (21), 6874–6887.
- (4) Rodrigues, T. S.; Zhao, M.; Yang, T. H.; Gilroy, K. D.; da Silva, A. G. M.; Camargo, P. H. C.; Xia, Y. Synthesis of Colloidal Metal Nanocrystals: A Comprehensive Review on the Reductants. *Chem. - A Eur. J.* **2018**, *24* (64), 16944–16963.
- (5) Ariga, K.; Ji, Q.; Hill, J. P.; Bando, Y.; Aono, M. Forming Nanomaterials as Layered Functional Structures toward Materials Nanoarchitectonics. *NPG Asia Mater.* **2012**, *4* (5), No. e17.
- (6) Li, X.; Wang, J. One-Dimensional and Two-Dimensional Synergized Nanostructures for High-Performing Energy Storage and Conversion. *InfoMat.* **2020**, *2* (1), 3–32.
- (7) Nguyen, T. D. From Formation Mechanisms to Synthetic Methods toward Shape-Controlled Oxide Nanoparticles. *Nanoscale* **2013**, *5* (20), 9455–9482.
- (8) Wu, Z.; Yang, S.; Wu, W. Shape Control of Inorganic Nanoparticles from Solution. *Nanoscale. Royal Soc. Chem.* **2016**, *21*, 1237–1259.

I

<https://doi.org/10.1021/acsami.5c07315>
ACS Appl. Mater. Interfaces XXXX, XXX, XXX–XXX

- (9) Davis, R.; Urbanowski, R. A.; Gaharwar, A. K. 2D Layered Nanomaterials for Therapeutics Delivery. *Curr. Opin. Biomed. Eng.* **2021**, *20* (June), 100319.
- (10) Lyu, Z.; Ding, S.; Du, D.; Qiu, K.; Liu, J.; Hayashi, K.; Zhang, X.; Lin, Y. Recent Advances in Biomedical Applications of 2D Nanomaterials with Peroxidase-like Properties. *Adv. Drug Delivery Rev.* **2022**, *185*, 114269.
- (11) Ariga, K.; Nishikawa, M.; Mori, T.; Takeya, J.; Shrestha, L. K.; Hill, J. P. Self-Assembly as a Key Player for Materials Nano-architectonics. *Sci. Technol. Adv. Mater.* **2019**, *20*, S1–95.
- (12) Zhu, Y.; Peng, L.; Fang, Z.; Yan, C.; Zhang, X.; Yu, G. Structural Engineering of 2D Nanomaterials for Energy Storage and Catalysis. *Adv. Mater.* **2018**, *30* (15), No. e1706347.
- (13) Baig, N.; Kammakam, I.; Falath, W. Nanomaterials: A Review of Synthesis Methods, Properties, Recent Progress, and Challenges. *Mater. Adv.* **2021**, *2*, 1821–1871.
- (14) Astruc, D. Introduction: Nanoparticles in Catalysis. *Chem. Rev.* **2020**, *120* (2), 461–463.
- (15) Feng, Y.; Yang, H.; Wang, X.; Hu, C.; Jing, H.; Cheng, J. Role of Transition Metals in Catalyst Designs for Oxygen Evolution Reaction: A Comprehensive Review. *Int. J. Hydrogen Energy* **2022**, *12*, 17946–17970.
- (16) Li, R.; Li, Y.; Yang, P.; Wang, D.; Xu, H.; Wang, B.; Meng, F.; Zhang, J.; An, M. Electrodeposition: Synthesis of Advanced Transition Metal-Based Catalyst for Hydrogen Production via Electrolysis of Water. *J. Energy Chem.* **2021**, *57*, S47–S66.
- (17) Suen, N. T.; Hung, S. F.; Quan, Q.; Zhang, N.; Xu, Y. J.; Chen, H. M. Electrocatalysis for the Oxygen Evolution Reaction: Recent Development and Future Perspectives. *Chem. Soc. Rev.* **2017**, *21*, 337–365.
- (18) Taylor, S. R. *Abundance of Chemical Elements in the Continental Crust: a New Table*; Pwgsmon Press Ltd, 1964; Vol. 28.
- (19) Hummer, D. R.; Golden, J. J.; Hystad, G.; Downs, R. T.; Eleish, A.; Liu, C.; Ralph, J.; Morrison, S. M.; Meyer, M. B.; Hazen, R. M. Evidence for the Oxidation of Earth's Crust from the Evolution of Manganese Minerals. *Nat. Commun.* **2022**, *13* (1), 1–7.
- (20) Song, J.; Wei, C.; Huang, Z. F.; Liu, C.; Zeng, L.; Wang, X.; Xu, Z. J. A Review on Fundamentals for Designing Oxygen Evolution Electrocatalysts. *Chem. Soc. Rev.* **2020**, *49* (7), 2196–2214.
- (21) Tian, T.; Gao, H.; Zhou, X.; Zheng, L.; Wu, J.; Li, K.; Ding, Y. Study of the Active Sites in Porous Nickel Oxide Nanosheets by Manganese Modulation for Enhanced Oxygen Evolution Catalysis. *ACS Energy Lett.* **2018**, *3* (9), 2150–2158.
- (22) Park, S.; Lee, Y. H.; Choi, S.; Seo, H.; Lee, M. Y.; Balamurugan, M.; Nam, K. T. Manganese Oxide-Based Heterogeneous Electrocatalysts for Water Oxidation. *Energy Environ. Sci.* **2020**, *1*, 2310–2340.
- (23) Tang, Y.; Zheng, S.; Cao, S.; Xue, H.; Pang, H. Advances in the Application of Manganese Dioxide and Its Composites as Electrocatalysts for the Oxygen Evolution Reaction. *J. Mater. Chem. A* **2020**, *8* (36), 18492–18514.
- (24) Ghosh, S. K. Diversity in the Family of Manganese Oxides at the Nanoscale: From Fundamentals to Applications. *ACS Omega* **2020**, *13*, 25493–25504.
- (25) Sun, W.; Kitchaev, D. A.; Kramer, D.; Ceder, G. Non-Equilibrium Crystallization Pathways of Manganese Oxides in Aqueous Solution. *Nat. Commun.* **2019**, *10* (1), 1–9.
- (26) Ding, B.; Zheng, P.; Ma, P.; Lin, J. Manganese Oxide Nanomaterials: Synthesis, Properties, and Theranostic Applications. *Adv. Mater.*; Wiley-VCH Verlag, 2020. *32*, 1905823.
- (27) Zhao, Q.; Song, A.; Ding, S.; Qin, R.; Cui, Y.; Li, S.; Pan, F. Preintercalation Strategy in Manganese Oxides for Electrochemical Energy Storage: Review and Prospects. *Adv. Mater.*, Wiley-VCH Verlag, 2020, *32*, 2002450.
- (28) Lourenço, A. A.; Silva, V. D.; da Silva, R. B.; Silva, U. C.; Chesman, C.; Salvador, C.; Simões, T. A.; Macedo, D. A.; da Silva, F. F. Metal-Organic Frameworks as Template for Synthesis of Mn³⁺/Mn⁴⁺ Mixed Valence Manganese Cobaltites Electrocatalysts for Oxygen Evolution Reaction. *J. Colloid Interface Sci.* **2021**, *582*, 124–136.
- (29) Beknalkar, S. A.; Teli, A. M.; Bhat, T. S.; Pawar, K. K.; Patil, S. S.; Harale, N. S.; Shin, J. C.; Patil, P. S. Mn₃O₄ Based Materials for Electrochemical Supercapacitors: Basic Principles, Charge Storage Mechanism, Progress, and Perspectives. *J. Mater. Sci. Technol.* **2022**, *10*, 227–248.
- (30) Kumbhar, V. S.; Lee, H.; Lee, J.; Lee, K. Recent Advances in Water-Splitting Electrocatalysts Based on Manganese Oxide. *Carbon Resour. Convers.* **2019**, *2* (3), 242–255.
- (31) He, R.; Yang, L.; Zhang, Y.; Jiang, D.; Lee, S.; Horta, S.; Zhifu Liang, Z.; Lu, X.; Ibáñez, J.; Li, M.; Zhou, Y.; Xu, Y.; Cabot, A. A 3d-4d-5d High Entropy Alloy as a Bifunctional Oxygen Catalyst for Robust Aqueous Zinc-Air Batteries. *Adv. Mater.* **2023**, *35* (46), 2303719.
- (32) Vij, V.; Sultan, S.; Harzandi, A. M.; Meena, A.; Tiwari, J. N.; Lee, W. G.; Yoon, T.; Kim, K. S. Nickel-Based Electrocatalysts for Oxygen-Related Applications: Oxygen Reduction, Oxygen Evolution, and Hydrogen Evolution Reactions. *ACS Catal.* **2017**, *7* (10), 7196–7225.
- (33) Jose, J.; Diana, E. J.; Kanchana, U. S.; Mathew, T. V. Recent Advances in the Nickel-Catalysed Electrochemical Coupling Reactions with a Focus on the Type of Bond Formed. *Asian J. Org. Chem.* **2023**, *12* (2), No. e202200593.
- (34) Kim, N.; Lim, D.; Choi, Y.; Shim, S. E.; Baek, S. H. Hexagonal β-Ni(OH)₂ Nanoplates with Oxygen Vacancies as Efficient Catalysts for the Oxygen Evolution Reaction. *Electrochim. Acta* **2019**, *324*, 134868.
- (35) Li, T.; Ma, X.; Wu, J.; Chu, F.; Qiao, L.; Song, Y.; Wu, M.; Lin, J.; Peng, L.; Chen, Z. Ni(OH)₂ Microspheres in Situ Self-Grown on Ultra-Thin Layered g-C₃N₄ as a Heterojunction Electrocatalyst for Oxygen Evolution Reaction. *Electrochim. Acta* **2021**, *400*, 139473.
- (36) Thenuwara, A. C.; Cerkez, E. B.; Shumlas, S. L.; Attanayake, N. H.; McKendry, I. G.; Frazer, L.; Borguet, E.; Kang, Q.; Remsing, R. C.; Klein, M. L.; Zdzila, M. J.; Strongin, D. R. Nickel Confined in the Interlayer Region of Birmessite: An Active Electrocatalyst for Water Oxidation. *Angew. Chem., Int. Ed.* **2016**, *128* (35), 10537–10541.
- (37) Zhou, X.; Xia, Z.; Zhang, Z.; Ma, Y.; Qu, Y. One-Step Synthesis of Multi-Walled Carbon Nanotubes/Ultra-Thin Ni(OH)₂ Nanoplate Composite as Efficient Catalysts for Water Oxidation. *J. Mater. Chem. A* **2014**, *2* (30), 11799–11806.
- (38) Heo, J. N.; Shin, J.; Yoon, T.; Son, N.; Kang, M. Effective Alkaline Water Electrolysis on NwMnO₂-NsNi(OH)₂ Composite Electrode via Lattice Oxygen Participant Adsorbate Evolving Mechanism. *Appl. Surf. Sci.* **2021**, *567*, 150281.
- (39) Selvakumar, K.; Duraisamy, V.; Venkateshwaran, S.; Arumugam, N.; Almansour, A. I.; Wang, Y.; Liu, T. X.; Kumar, S. M. S. Development of α-MnO₂ Nanowire with Ni- and (Ni, Co)-Cation Doping as an Efficient Bifunctional Oxygen Evolution and Oxygen Reduction Reaction Catalyst. *ChemElectrochem* **2022**, *9* (2), No. e202101303.
- (40) Nagajyothi, P. C.; Ramaraghavulu, R.; Munirathnam, K.; Yoo, K.; Shim, J. One-Pot Hydrothermal Synthesis: Enhanced MOR and OER Performance Using Low-Cost Mn₃O₄ Electrocatalyst. *Int. J. Hydrogen Energy* **2021**, *46* (27), 13946–13951.
- (41) Li, P.; Nan, C.; Wei, Z.; Lu, J.; Peng, Q.; Li, Y. Mn₃O₄ Nanocrystals: Facile Synthesis, Controlled Assembly, and Application. *Chem. Mater.* **2010**, *22* (14), 4232–4236.
- (42) Cheng, Y.; Wei, Z.; Du, Q.; Liu, F.; Duan, X.; Wang, Y.; Jia, D.; Zhou, Y.; Li, B. The Shape Effect of Manganese(II,III) Oxide Nanoparticles on the Performance of Electrochemical Capacitors. *Electrochim. Acta* **2018**, *284*, 408–417.
- (43) Dinesh, M.; Haldorai, Y.; Rajendra Kumar, R. T. Mn–Ni Binary Metal Oxide for High-Performance Supercapacitor and Electro-Catalyst for Oxygen Evolution Reaction. *Ceram. Int.* **2020**, *46* (18), 28006–28012.
- (44) Cossar, E.; Houache, M. S. E.; Zhang, Z.; Baranova, E. A. Comparison of Electrochemical Active Surface Area Methods for

Various Nickel Nanostructures. *J. Electroanal. Chem.* **2020**, *870*, 114246.

(45) Wang, X.; Han, X.; Du, R.; Liang, Z.; Zuo, Y.; Guardia, P.; Li, J.; Llorca, J.; Arbiol, J.; Zheng, R.; Cabot, A. Unveiling the Role of Counter-Anions in Amorphous Transition Metal-Based Oxygen Evolution Electrocatalysts. *Appl. Catal., B* **2023**, *321*, 219880.

(46) Li, J.; Wang, X.; Xing, C.; Li, L.; Mu, S.; Han, X.; He, R.; Liang, Z.; Martinez, P.; Yi, Y.; Wu, Q.; Pan, H.; Arbiol, J.; Cui, C.; Zhang, Y.; Cabot, A. Electrochemical Reforming of Ethanol with Acetate Co-Production on Nickel Cobalt Selenide Nanoparticles. *Chem. Eng. J.* **2022**, *440* (2021), 135817.

(47) Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys. Rev. B* **1996**, *54* (16), 11169–11186.

(48) Blochl, P. E. Projector Augmented-Wave Method. *Phys. Rev. B* **1994**, *50*, 17953–17979.

(49) Dudarev, S.; Botton, G.; Savrasov, S. Y.; Humphreys, C. J.; Sutton, A. P. Electron-Energy-Loss Spectra and the Structural Stability of Nickel Oxide: An LSDA+U Study. *Phys. Rev. B* **1998**, *57* (3), 1505–1509.

(50) Wang, L.; Maxisch, T.; Ceder, G. Oxidation Energies of Transition Metal Oxides within the GGA+U Framework. *Phys. Rev. B* **2006**, *73* (19), 195107.

(51) Monkhorst, H. J.; Pack, J. D. "special Points for Brillouin-Zone Integrations"-a Reply. *Phys. Rev. B* **1977**, *16* (4), 1748–1749.

(52) Norskov, J. K.; Rossmeisl, J.; Logadottir, A.; Lindqvist, L.; Kitchin, J. R.; Bligaard, T.; Jönsson, H. Origin of the Overpotential for Oxygen Reduction at a Fuel-Cell Cathode. *J. Phys. Chem. B* **2004**, *108* (46), 17886–17892.

(53) Morris, T.; Zubkov, T. Steric Effects of Carboxylic Capping Ligands on the Growth of the CdSe Quantum Dots. *Colloids Surf., A* **2014**, *443*, 439–449.

(54) Si, K. J.; Chen, Y.; Shi, Q.; Cheng, W. Nanoparticle Superlattices: The Roles of Soft Ligands. *Adv. Sci.* **2018**, *5*, 1700179.

(55) Mozaffari, S.; Li, W.; Dixit, M.; Seifert, S.; Lee, B.; Kovarik, L.; Mpourmpakis, G.; Karim, A. M. The Role of Nanoparticle Size and Ligand Coverage in Size Focusing of Colloidal Metal Nanoparticles. *Nanoscale Adv.* **2019**, *1* (10), 4052–4066.

(56) Yang, T.-H.; Shi, Y.; Janssen, A.; Xia, Y. Surface Capping Agents and Their Roles in Shape-Controlled Synthesis of Colloidal Metal Nanocrystals. *Angew. Chem. Internat.* **2020**, *59*, 15378–15401.

(57) Fereshteh, Z.; Salavati-Niasari, M. Effect of Ligand on Particle Size and Morphology of Nanostructures Synthesized by Thermal Decomposition of Coordination Compounds. *Adv. Colloid Interface Sci.* **2017**, *243*, 86–104.

(58) Thanh, N. T. K.; Maclean, N.; Mahiddine, S. Mechanisms of Nucleation and Growth of Nanoparticles in Solution. *Chem. Rev.* **2014**, *114* (15), 7610–7630.

(59) Zhang, P.; Li, L.; Nordlund, D.; Chen, H.; Fan, L.; Zhang, B.; Sheng, X.; Daniel, Q.; Sun, L. Dendritic Core-Shell Nickel-Iron-Copper Metal/Metal Oxide Electrode for Efficient Electrocatalytic Water Oxidation. *Nat. Commun.* **2018**, *9* (1), 1–10.

(60) Wei, C.; Rao, R. R.; Peng, J.; Huang, B.; Stephens, I. E. L.; Risch, M.; Xu, Z. J.; Shao-Horn, Y. Recommended Practices and Benchmark Activity for Hydrogen and Oxygen Electrocatalysis in Water Splitting and Fuel Cells. *Adv. Mater.* **2019**, *31* (31), 1–24.

(61) Wei, C.; Sun, S.; Mandler, D.; Wang, X.; Qiao, S. Z.; Xu, Z. J. Approaches for Measuring the Surface Areas of Metal Oxide Electrocatalysts for Determining Their Intrinsic Electrocatalytic Activity. *Chem. Soc. Rev.* **2019**, *48* (9), 2518–2534.

(62) Sun, S.; Li, H.; Xu, Z. J. Impact of Surface Area in Evaluation of Catalyst Activity. *Joule* **2018**, *2* (6), 1024–1027.

(63) He, Y.; Kang, Z.; Li, J.; Li, Y.; Tian, X. Recent Progress of Manganese Dioxide Based Electrocatalysts for the Oxygen Evolution Reaction. *Ind. Chem. Mater.* **2023**, *1* (3), 312–331.

(64) Rajput, A.; Kumari, A.; Basak, H. K.; Ghosh, D.; Chakraborty, B. Tracking the Active Phase and Reaction Pathway of the OER

Mediated by an MnMoO₄ Microrod Electro(Pre)-Catalyst. *J. Mater. Chem. A* **2024**, *12*, 30810–30820.

(65) Meng, Y.; Song, W.; Huang, H.; Ren, Z.; Chen, S. Y.; Suib, S. L. Structure-Property Relationship of Bifunctional MnO₂ Nanostructures: Highly Efficient, Ultra-Stable Electrochemical Water Oxidation and Oxygen Reduction Reaction Catalysts Identified in Alkaline Media. *J. Am. Chem. Soc.* **2014**, *136* (32), 11452–11464.

(66) Zhang, Y.; Zhang, H.; Fang, L.; Deng, J.; Wang, Y. Facile Synthesis of Nickel Manganese Composite Oxide Nanomesh for Efficient Oxygen Evolution Reaction and Supercapacitors. *Electrochim. Acta* **2017**, *245*, 32–40.

(67) Bhagwan, J.; Nagaraju, G.; Ramulu, B.; Sekhar, S. C.; Yu, J. S. Rapid Synthesis of Hexagonal NiCo₂O₄ Nanostructures for High-Performance Asymmetric Supercapacitors. *Electrochim. Acta* **2019**, *299*, 509–517.

(68) Hussain, S. K.; Nagaraju, G.; Sekhar, S. C.; Yu, J. S. S. Morphological Synergistic Behavior on Electrochemical Performance of Battery-Type Spinel Nickel Manganese Oxides for Aqueous Hybrid Supercapacitors. *J. Power Sources* **2019**, *439*, 227088.

(69) Lima, F. H. B.; Calegari, M. L.; Ticianelli, E. A. Electrocatalytic Activity of Manganese Oxides Prepared by Thermal Decomposition for Oxygen Reduction. *Electrochim. Acta* **2007**, *52* (11), 3732–3738.

(70) Rani, B. J.; Ravi, G.; Yuvakkumar, R.; Hong, S. I.; Velauthapillai, D.; Thambidurai, M.; Dang, C.; Saravanakumar, B. Neutral and Alkaline Chemical Environment Dependent Synthesis of Mn₂O₄ for Oxygen Evolution Reaction (OER). *Mater. Chem. Phys.* **2020**, *247* (2019), 122864.

(71) Li, M.; Wang, X.; Zhang, D.; Huang, Y.; Shen, Y.; Pan, F.; Lin, J.; Yan, W.; Sun, D.; Huang, K.; Tang, Y.; Lee, J. M.; Li, H.; Fu, G. Atomic Rare Earths Activate Direct O-O Coupling in Manganese Oxide towards Electrocatalytic Oxygen Evolution. *Nano Energy* **2024**, *128* (PA), 109868.

(72) Ciano, R.; Dunin-Borkowski, R. E.; Snoeck, E.; Kociak, M.; Holmestad, R.; Verbeeck, J.; Kirkland, A. L.; Kothleitner, G.; Arbiol, J. *Microsc. Microanal.* **2022**, *28*, 2900–2902.



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Active site switching on high entropy phosphides as bifunctional oxygen electrocatalysts for rechargeable/robust Zn–air battery†

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High-entropy materials (HEMs) offer a quasi-continuous spectrum of active sites and have generated great expectations in fields such as electrocatalysis and energy storage. Despite their potential, the complex composition and associated surface phenomena of HEMs pose challenges to their rational design and development. In this context, we have synthesized FeCoNiPdW high entropy phosphide (HEP) nanoparticles using a low-temperature colloidal method, and explored their application as bifunctional electrocatalysts for the oxygen evolution and reduction reactions (OER/ORR). Our analysis provides a detailed understanding of the individual roles and transformations of each element during OER/ORR operation. Notably, the HEPs exhibit an exceptionally low OER overpotential of 227 mV at 10 mA cm⁻², attributed to the reconstructed HEP surface into a FeCoNiPdW high entropy oxyhydroxide with high oxidation states of Fe, Co, and Ni serving as the active sites. Additionally, Pd and W play crucial roles in modulating the electronic structure to optimize the adsorption energy of oxygen intermediates. For the ORR, Pd emerges as the most active component. In the reconstructed catalyst, the strong d–d orbital coupling of especially Pd, Co, and W fine-tunes ORR electron transfer pathways, delivering an ORR half-wave potential of 0.81 V with a pure four-electron reduction mechanism. The practicality of these HEPs catalysts is showcased through the assembly of aqueous zinc–air batteries. These batteries demonstrate a superior specific capacity of 886 mA h g_{Zn}⁻¹ and maintain excellent stability over more than 700 hours of continuous operation. Overall, this study not only elucidates the role of each element in HEMs but also establishes a foundational framework for the design and development of next-generation bifunctional oxygen catalysts, broadening the potential applications of these complex materials in advanced energy systems.

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Broader context

Rechargeable zinc–oxygen batteries represent a cutting-edge technology with promising applications ranging from large-scale stationary energy storage for renewable energy integration to powering electric vehicles and small-scale wearable devices. However, their performance is limited by the slow kinetics of oxygen redox reactions at the oxygen cathode, which significantly restricts their practical utility. To address these challenges, there is a pressing need for a new generation of oxygen redox catalysts. High entropy materials are emerging as powerful bifunctional oxygen electrocatalysts due to their quasi-continuous distribution of surface energy levels and the extensive flexibility they offer in tuning surface compositions. These properties are crucial for optimizing the adsorption energies of reactants, intermediates, and products involved in the redox processes. In this study, we present a solution-based synthesis route for producing FeCoNiPdWP nanoparticles, and demonstrate them to show outstanding combined performance in both oxygen reduction and evolution reactions. Besides, we have conducted a thorough investigation into the specific roles that each metal element plays in the redox process. Additionally, these high entropy phosphide nanoparticles are integrated as the air cathode in rechargeable zinc–air batteries, resulting in devices that exhibit unprecedented performance and stability.

1. Introduction

Rechargeable aqueous zinc–air batteries (ZABs) are recognized for their exceptional energy densities, inherent safety, sustainability, and potential for cost-effectiveness across various applications, including electric vehicles and large-scale stationary energy storage systems.¹ However, the performance of ZABs strongly relies on the activity, stability, and cost of the oxygen catalyst used at the cathode side to boost the oxygen evolution and reduction reactions (OER, ORR) during battery charging and discharging, respectively.^{2–4}

For decades, significant efforts have been directed toward developing high-performance bifunctional oxygen electrocatalysts. Traditionally, a physical mixture of noble metal catalysts, *e.g.* Pt/C for ORR and Ir/C for OER, has been used to accelerate the kinetics of the two reactions. Despite their relative effectiveness, the high cost, the scarcity of these noble metals, and the need to double the catalyst amount—since each material facilitates only one type of reaction—pose substantial barriers to the commercial viability of ZABs.^{5–8} To address this limitation, alternative bifunctional oxygen catalysts based on layered double hydroxides,⁹ perovskites,¹⁰ metallic alloys,¹¹ sulfides,¹² nitrides,¹³ phosphides,¹⁴ and their composites^{15–17} are intensively investigated.

Electrocatalysts based on high-entropy materials (HEMs) have emerged as particularly promising due to their vast compositional versatility and the ability to finely tune their surface properties to optimize performance. Their complex composition and a huge amount of different potential surface configurations also result in quasi-continuous surface energy levels able to suit the adsorption of reactants, intermediates, and products, facilitating enhanced catalytic activities across various reactions.^{18–23} The diverse range of surface sites provided by HEMs makes them ideal for catalyzing complex reactions and especially valuable as bifunctional catalysts. Despite these advantages, achieving a single HEM that excels in both OER and ORR remains a formidable challenge, primarily due to the divergent pathways and distinct intermediate adsorption energies required by these reactions.^{24,25}

The vast range of potential HEM compositions makes trial-and-error processes hopeless to optimize them as dual-functional catalysts. Thus, to avoid a futile odyssey across the boundless expanse of HEMs, an educated selection of the HEMs characteristics leading to optimized catalytic performance is fundamental. This rational design must be supported by reliable structure–

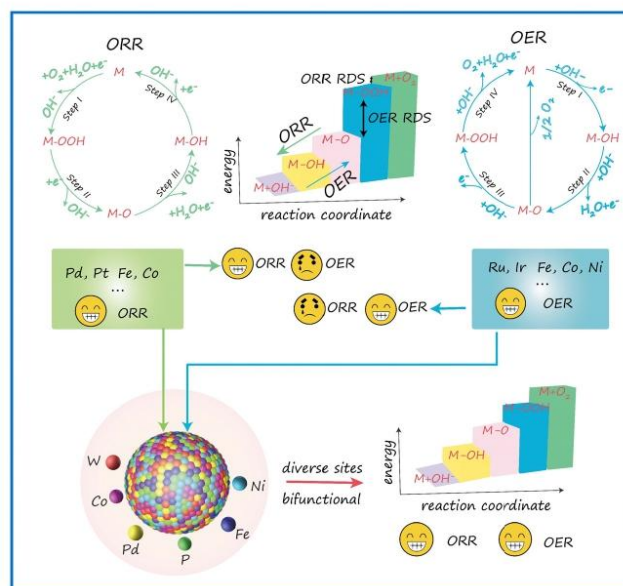
activity relationships and precise information on the distinct roles of each element in the OER and ORR mechanisms. However, gathering this information is especially difficult for HEMs having hundreds of thousands of possible atomic configurations. Besides, further complications arise with inevitable surface reconstructions caused by the strongly alkaline reaction conditions used.^{26,27} Therefore, it is essential to delve into the catalyst reconstruction and explore the unique contributions of each metal involved. This approach is crucial for a holistic comprehension of the intricate dynamics at play within HEMs during catalysis.

Herein, FeCoNiPdWP high entropy phosphide (HEP) nanoparticles are synthesized using a mild colloidal method. Subsequently, their OER and ORR performance is compared with a series of control phosphides and commercial reference catalysts. To gain deeper insights into the oxygen redox reaction mechanisms, the distinct roles played by each metal in HEPs are analyzed using electrochemical measurements, X-ray absorption spectroscopy (XAS), and density functional theory (DFT) calculations. Furthermore, the HEP surface reconstruction and the real active species are explored and identified. Last, rechargeable ZABs based on FeCoNiPdWP HEPs bifunctional oxygen catalysts as the air cathodes are assembled and tested.

2. Results and discussion**2.1 Design principles of HEP**

A primary challenge in developing bifunctional catalysts for OER/ORR is ensuring the availability of proper catalytic sites. As illustrated in Scheme 1, an effective catalyst typically provides surface sites that strongly adsorb reactants and intermediates but only weakly bind to the products, thereby promoting high efficiency in driving the forward reaction. In contrast, this type of catalyst often shows much lower efficiency for the reverse reaction. The opposite is true for catalysts that favor strong adsorption of the products. HEMs offer a promising solution to this challenge. These materials combine a vast array of different active sites, providing a continuum of adsorption energies. This unique feature enables HEMs to efficiently catalyze both OER and ORR, making them highly effective as bifunctional oxygen catalysts.

Transition metal phosphides have attracted substantial attention due to their metallic character and associated high electrical conductivity, as well as their abundant reserves, cost-effectiveness, and stability.^{28–32} The higher electronegativity of



Scheme 1 Schematic illustration of the design principles of FeCoNiPdWP HEPs as bifunctional oxygen catalysts in an alkaline electrolyte.

phosphorus than transition metals triggers electron delocalization and leads to partially positively charged metal and negatively charged phosphorus, where transition metals could serve as the OH^- acceptor to modulate the binding ability for OER/ORR. From the electronic band structure perspective, the presence of phosphorus modifies the electronic energy levels and d-band center, increasing the density-of-states near the Fermi level,³³ which signifies abundant charge carriers similar to the noble metals for the OER/ORR process, thus frequently improving electrocatalytic performance.^{34–36} In addition, the covalent nature of the metal–phosphorus bond promotes the durability and long-term stability of the electrocatalysts. Indeed, the hybridization of d metal orbitals with the p orbital of P to form metal–phosphorus bonds has been demonstrated to be beneficial in boosting ORR performance.³⁰ Therefore, the rational design and engineering of HEPs for ZAB applications is a worthy endeavor.

Based on our previous study, the combination of 3d/4d/5d metals significantly modulates the electronic state and surface electron density, altering the bond strength between the metal and oxygen species, which allows adjusting the adsorption/desorption ability of intermediates and products.^{18,37,38} The d orbitals of 5d metals are more extended and have higher energy and spatial coverage compared to those of 3d/4d metals. When 5d metals combine with 3d metals, hybrid orbitals are formed, adjusting the electron distribution and orbital overlap, thereby potentially providing more active sites and enhancing catalytic activity. The high electronegativity of the 5d metals allows for the regulation of the electron-filling states of the 3d/4d metals, optimizing the surface electronic structure of the catalysts.

In addition, 5d metals provide strong electronic attraction and create new coordination environments, stabilizing reaction intermediates, and reducing poisoning. Thus, W, a 5d metal with a unique orbital filling state was incorporated into the HEP catalyst.

In terms of the 3d transition metals, Fe, Co, and Ni were selected as well-established effective OER active sites based on their cost-effectiveness, the theoretically calculated volcano graph curves between overpotential and intrinsic catalytic activity,^{39–43} and their rich valence state transitions, abundant electronic configuration, and adjustable spin state, which could effectively regulate the binding energy and modulate the spin flipping of the oxygen intermediates.^{44,45} On the other hand, while a large number of excellent ORR catalysts have been reported, the most effective catalysts are still based on Pt and Pd. Therefore, Pd was incorporated into the HEP to promote ORR performance.^{46,47} Besides, Pd easily forms alloys with other transition metals,⁴⁸ facilitating the HEP formation. Notice also that within an HEM, the amount of Pd is minimized compared with catalysts based on elemental Pd or binary Pd-based alloys. Overall, FeCoNiPdWP HEPs are expected to simultaneously provide superior OER and ORR performance with expectable W-modulated Fe/Co/Ni as the OER active sites and Pd as the ORR active sites, making them a potentially ideal cathode material in ZABs.

2.2 HEP synthesis and characterization

FeCoNiPdWP HEPs and the related reference quaternary metal phosphides (FeCoNiPdP, FeCoPdWP, CoNiPdWP, FeNiPdWP, and FeCoNiWP) were synthesized using a heating-up colloidal synthesis approach (Fig. 1a) using a mixture of 1-octadecene and

oleylamine as the solvent (see details in the experimental section in the ESI†). Triphenyl phosphite was selected as a low-cost, safe, and stable phosphorus source.^{49–51} Metal acetylacetonates and carbonyls were used as metal precursors. The reaction temperature was set to 290 °C. At this temperature, the phosphorus–oxygen bonds in triphenyl phosphite molecules are cleaved, releasing phosphorous atoms that react with the metal precursors to yield the HEP. Fig. S1–S6 (ESI†) show the results from the characterisation of the reference quaternary metal phosphides.

Transmission electron microscope (TEM) images show the FeCoNiPdWP HEP nanoparticles to have an average size of 20 nm (Fig. 1b). Spherical aberration-corrected high-resolution TEM (AC-HRTEM) analysis confirmed their high crystallinity (Fig. 1c and d). X-Ray diffraction (XRD) pattern determined the particles to have the Pd₁₅P₂ rhombohedral phase (JCPDS 01-071-0193) (Fig. S6a, ESI†). Geometric phase analysis (GPA) shows a random distribution of distortions induced by tensile and compressive stresses attributed to the different atomic

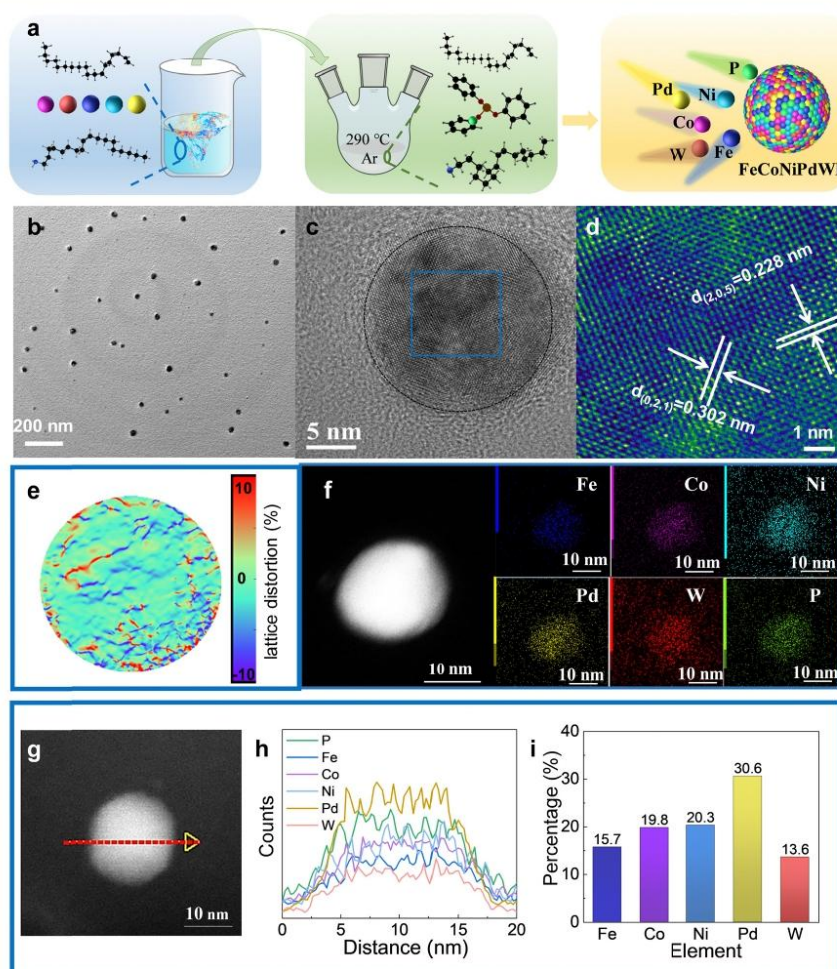


Fig. 1 Chemical and structural characterization of FeCoNiPdWP nanoparticles. (a) Scheme of the synthesis approach used to produce FeCoNiPdWP HEPs. (b) TEM image. (c) AC-HRTEM image. (d) Magnified AC-HRTEM image and lattice distance analysis of the blue square in (c). Two crystal planes with lattice distances of 0.228 and 0.302 nm are indexed to the (205) and (021) crystal planes of the Pd₁₅P₂ rhombohedral phase, respectively. (e) GPA analysis. (f) HAADF-STEM micrograph and EDS compositional maps. (g) HAADF-STEM micrograph and (h) line scanning profiles. (i) Metal ratios obtained using ICP-OES.

radii and electronegativity of the constituent elements (Fig. 1e). High-angle annular dark field scanning TEM (HAADF-STEM) micrographs combined with energy-dispersive X-ray spectroscopy (EDS) compositional maps show a homogeneous distribution of the different elements within the HEP nanoparticles (Fig. 1f-h). The TEM-EDS metal ratios are consistent with those obtained from inductively coupled plasma optical emission spectroscopy (ICP-OES): Fe/Co/Ni/Pd/W = 15.7/19.8/20.3/30.6/13.6 (Fig. 1i).

2.3 OER

2.3.1 OER catalytic performance. The OER activity of the materials supported on glassy carbon (GC) was evaluated by linear sweep voltammetry (LSV) in 1.0 M KOH (see the experimental section in the ESI† for electrode preparation and OER test details). The LSV curves display a small bump in the potential range of 1.3–1.4 V vs. RHE associated with the oxidation of the transition metals. FeCoNiPdWP shows the best OER catalytic performance with outstanding low overpotentials of 227 mV at 10 mA cm⁻², 250 mV at 50 mA cm⁻², and 258 mV at

100 mA cm⁻² (Fig. 2a and b). These values are well below those measured for RuO₂, PdP_x (Fig. S7, ESI†), and the quaternary phosphides, which overpotential at 10/100 mA cm⁻² follows the trend FeCoNiPdWP < FeCoNiPdP < FeNiPdWP < FeCoPdWP < FeCoNiWP < CoNiPdWP < RuO₂ < PdP_x (Fig. S8, ESI†).

FeCoNiPdWP also shows the smallest Tafel slope (33 mV dec⁻¹), well below that of the other metal phosphides (37–59 mV dec⁻¹) and RuO₂ (75 mV dec⁻¹), demonstrating especially favorable OER kinetics (Fig. 2c). Cyclic voltammetry (CV) curves at different scan rates (Fig. S9, ESI†) and the derived double-layer capacitance (*C*_{dl}) values (Fig. 2d) show that all the quaternary and quinary phosphide catalysts have a similar electrochemical active surface area (ECSA), higher than that of PdP_x (Fig. S10, ESI†). Normalization of the OER current densities by the ECSA values implies that FeCoNiPdWP has a higher intrinsic activity per active site (Fig. 2e). Electrochemical impedance spectroscopy (EIS) analysis confirms FeCoNiPdWP to display the smallest OER charge transfer impedance thus the most favorable reaction kinetics (Fig. 2f and Table S1, ESI†).

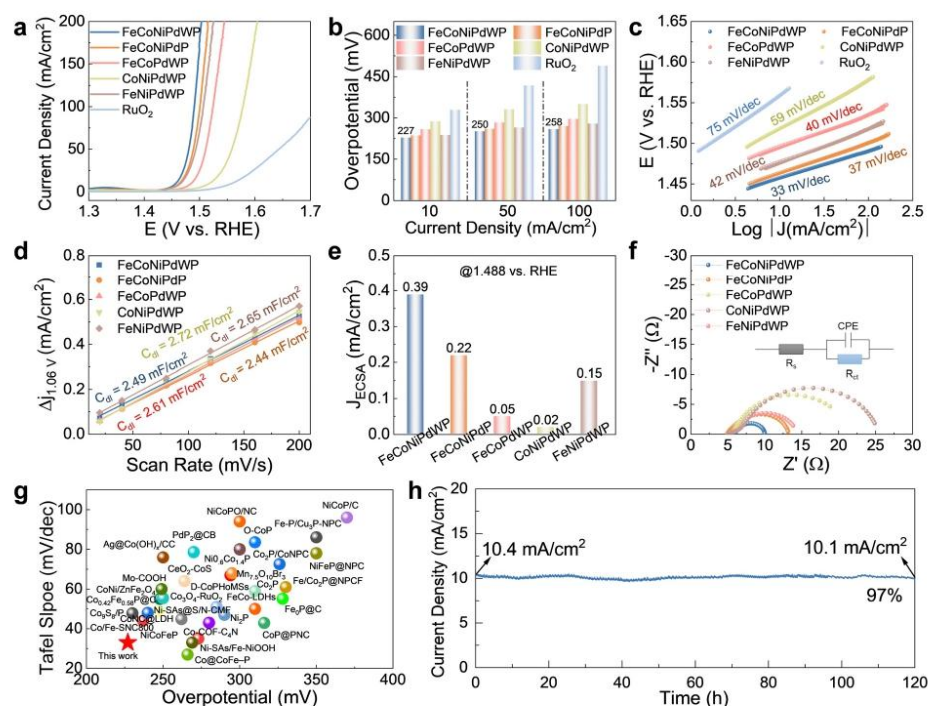


Fig. 2 OER performance on GC electrodes with a loading of 0.5 mg cm⁻². (a) LSV curves at 5 mV s⁻¹. (b) Overpotential at different current densities. (c) Tafel fitting plots calculated from the LSV curves in (a), the open circles are measured data and the long solid lines are fitted data. (d) *C*_{dl} values calculated from the CV curves in Fig. S9 (ESI†). (e) Current density normalized by ECSA at 1.488 vs. RHE. (f) Nyquist plot of the EIS spectra of the different catalysts at 1.5 V vs. RHE. The inset shows the equivalent circuit model used to fit the experimental data (Table S1, ESI†), where *R*_s is the internal resistance of the cell, *R*_{ct} is the charge-transfer resistance, and CPE represents the double-layer capacitance at the electrode-electrolyte interphase. (g) Comparisons of the OER performance of FeCoNiPdWP with other recently reported catalysts on GC. (h) CA curve of FeCoNiPdWP at 1.46 V vs. RHE.

Overall, FeCoNiPdWP HEPs show superior OER performance when compared not only with the reference materials tested here but also with previously reported catalysts supported on GC, as shown in Fig. 2g and Table S2 (ESI†).^{4,52–84} Besides, FeCoNiPdWP shows excellent stability with a continuously applied potential of 1.46 V vs. RHE for 120 h resulting in just a 3% decrease in current density as determined by chronoamperometry (CA) measurements (Fig. 2h), well below the current density decay obtained from the quaternary metal phosphides (Fig. S11, ESI†).

2.3.2 HEP reconstruction during OER. The high-resolution X-ray photoelectron spectroscopy (XPS) spectra of FeCoNiPdWP HEPs before and after OER operation are displayed in Fig. S12 and S13 (ESI†). Before OER, FeCoNiPdWP displays both M–P and M–O surface chemical environments, the latter originated during sample storage, transportation, and manipulation.^{85,86} After long-term OER, surface metals show a single oxidation state, Fe³⁺, Co²⁺, Ni³⁺, and W⁶⁺, with no M–P chemical environment. Besides, no P is detected at the surface of the HEP nanoparticles. Additionally, the hydroxide (O_{OH}) contribution to the O 1s XPS spectrum becomes dominant, which is attributed to the formation of a metal (oxy)hydroxide surface.

XRD analysis of FeCoNiPdWP after the OER stability test revealed that the crystalline Pd₁₅P₂ rhombohedral phase disappeared during OER operation (Fig. S14, ESI†). Besides, EDS spectra (Fig. S15 and S16, ESI†) show that the P amount strongly decreased from 29% to 3% after OER. *In situ* Raman spectroscopy was used to explore the evolution of HEP with the applied potential (Fig. S17, ESI†). The spectra show Raman peaks at around 300 cm^{−1}, and 400–700 cm^{−1}, whose intensity increases with the applied voltage. This observation is related to the formation of layered Fe/Co/Ni (oxy)hydroxides.^{87,88} Thus, overall, XPS, XRD, and Raman results are consistent with the HEP being reconstructed into a high entropy oxyhydroxide (HEOOH) in OER conditions.

XAS on the Fe, Co, Ni K-edge was used to gain an understanding of the FeCoNiPdWP atomic structure and the reconstruction process taking place during OER for the as-prepared HEP nanoparticles, the fresh electrode, and the electrode with the completed reconstruction process. X-ray absorption near edge spectroscopy (XANES) analysis of the reconstructed samples revealed significant increases in the oxidation states of the metals during OER operation, with Fe increasing from 3.0 to

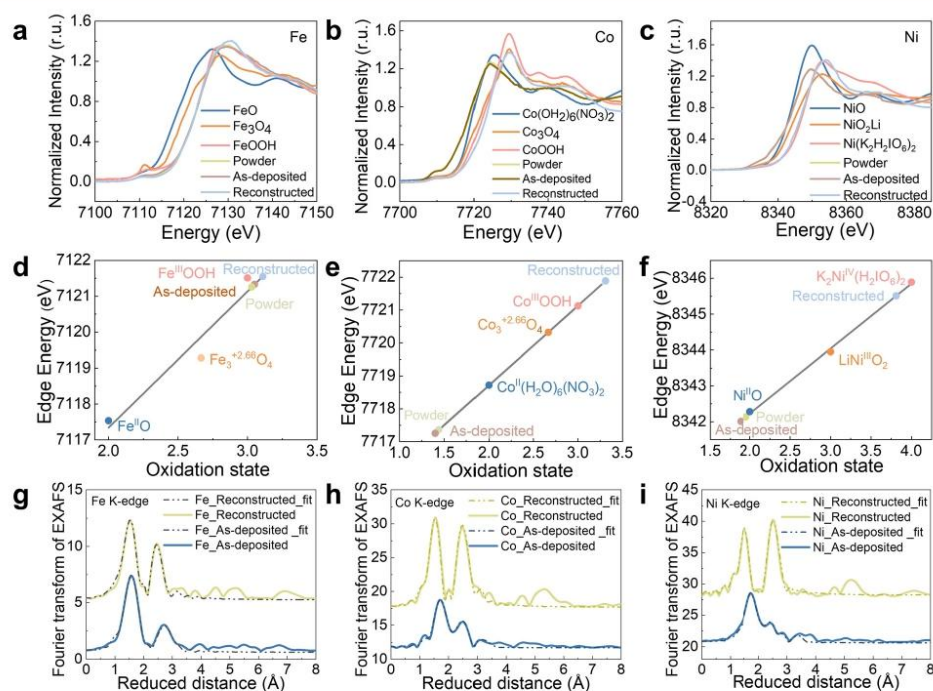


Fig. 3 XAS characterization of HEPs. (a)–(c) Fe (a), Co (b), and Ni (c) XANES plots of the as-prepared powders, the as-deposited films, and reconstructed films, freeze-quenched at 153 V vs. RHE after 2 h OER operation. (d)–(f) Metal oxidation states of Fe (d), Co (e), and Ni (f) from the XANES. To quantify differences in the edge positions, the K-edge energy was calculated using the integral method,⁹⁵ and the obtained values are plotted here as symbols. A linear regression including the three iron/cobalt/nickel oxide references was used to derive the oxidation states of the HEPs before and during the OER. (g)–(i) Fe (g), Co (h), and Ni (i) EXAFS spectra (Fig. S18, ESI†) and simulations (Table S4 for the simulation parameters, ESI†). The data at the bottom/up show the as-prepared/reconstructed electrodes.

3.1, Co from 1.4 to 3.3, and Ni from 2.0 to 3.8 (Fig. 3a–f and Table S3, ESI†). Fe, Co, and Ni in oxidation states above three have been shown to facilitate water oxidation.^{89–94} Thus, the high Fe, Co, and Ni average oxidation states during the OER support the hypothesis that these three elements or their multimetallic neighbouring sites function as OER active sites.

To gain insight into the local structure of Fe/Co/Ni, the extended X-ray absorption fine structure (EXAFS) data and k^3 -weighted EXAFS spectra were simulated, as shown in Fig. 3g–i and Fig. S18 (ESI†). For all the 3d metals, models of layers with edge-sharing $[\text{MO}_6]$ octahedra were applied to simulate the EXAFS spectra (see Table S4 for fitting parameters, ESI†). The model comprises three shells: (i) for the M–O bond of the $[\text{MO}_6]$ octahedra (1.87–2.02 Å), (ii) for the M–M distance of two adjacent $[\text{MO}_6]$ octahedra (2.81–2.98 Å), and (iii) a second, larger M–O distance (3.40–3.43 Å). This model is consistent with the FeCoNi oxyhydroxide structure or their deprotonated, oxidized, and potassium-intercalated relatives that have recently been proposed to form during OER.⁹⁴ For Fe, two M–O bond distances (1.89 and 2.02 Å) were required, likely due to the presence of a Jahn–Teller distortion caused by the unevenly occupied t_{2g} orbital of $[\text{Fe}^{\text{III}}\text{O}_6]$. The presence of two different M–O bond lengths automatically leads to two different Fe–M bond distances as well, which were taken into account in the simulation. The short M–O bond distances (1.87–1.89 Å) are consistent with the high oxidation states extracted from the XANES data (Table S4, ESI†). Overall, results from XAS analyses reveal that, during OER, FeCoNiPdWP is fully reconstructed into layers of edge-sharing $[\text{MO}_6]$ octahedra with 3d metal oxidation states above three. These motifs are consistent with highly oxidized oxyhydroxides and related structures that are frequently observed during and after the OER.^{94,96–98}

2.3.3 HEP element roles in OER. DFT calculations were carried out to identify the roles of individual metal sites and their synergistic effects in the FeCoNiPdWP HEPs reconstructed during the OER, denoted as FeCoNiPdWOOH (Fig. S19, ESI†), and the reference reconstructed quaternary compounds (Fig. S20–S25, ESI†). As shown in Fig. 4a, all the reconstructed models have the Fermi level (E_F) within a band of states, indicating a metallic conductivity. The total density of state (TDOS) of FeCoNiPdWOOH is greater than that of the reference compounds at around E_F , pointing to a higher electron transport rate. The projected DOS (PDOSs) of each element in the FeCoNiPdWOOH model is displayed in Fig. 4b. Notably, the O 2p orbitals have a strong overlap with the different metal elements, pointing at an efficient p–d orbital coupling and self-complementary effect.⁹⁹ The Ni-3d and Co-3d orbitals are close to E_F , pointing to high electrochemical activity with strong electron depletion capability. The Fe-3d orbital shows e_g – t_{2g} splitting with a strong overlap with the W 5d orbitals, implying a high degree of W 5d–Fe 3d orbital coupling and electron exchange between these two metals.^{100,101} The center of the Pd-4d band is located well below the E_F , lower than the other metal sites, indicating an electron-rich characteristic. Consistently, the charge density difference (CDD) analysis revealed that Pd sites exhibit electron accumulation (Fig. S20b, ESI†). In addition, Pd-4d orbitals cover a wide energy range, from –10.0 eV to E_F . Overall,

Fe-3d, Co-3d, Ni-3d, Pd-4d, W-5d, and O-2p orbitals cross the E_F and show a significant covalent interaction between metal and O bands, which boosts the site-to-site electron transfer and might be one of the reasons for the outstanding OER performance of the reconstructed HEOOH. Meanwhile, the d-band center (d_c) of FeCoNiPdWOOH is higher than that of the quaternary metal oxyhydroxides and the electronic structure balance involves charge transfer between all the different elements (Fig. 4c).

PDOS analysis was used to evaluate the adsorption behaviors over different sites. For the reactant OH^- species, during the initial adsorption process, s/p bands were down-shifted (Fig. 4d), indicating electron transfer from the surface sites to OH^- to stabilize adsorbed $^*\text{OH}$. The improved adsorption capability favored the weakening of O–H bonds in $^*\text{OH}$, thus triggering the subsequent dissociation processes. Compared with Fe, Co, and W sites, stronger p–d orbital couplings between the OH^* and Ni/Pd sites were observed, which points to a more stable adsorption of OH^* on the Ni/Pd sites within FeCoNiPdWOOH. This was experimentally demonstrated by the methanol probe molecule test of FeCoNiPdWP and FeCoNiWP in 1 M KOH and 1 M methanol, concluding that the presence of Pd significantly promoted the adsorption of OH^- species (Fig. S26, ESI†). CDD results also showed that Ni sites presented noticeable electron depletion with OH^- adsorption, demonstrating charge transfer during the adsorbing process (Fig. S27, ESI†). The integral projected crystal orbital Hamilton population value (ICOHP) provides the number of bonded electrons between the selected metal and O atoms in the active $^*\text{OH}$ and the corresponding bonding strength. Notably, the ICOHPs of Ni and Pd are larger than those of Fe/Co/W, demonstrating stronger OH adsorption in the formers (Fig. 4e).

Gibbs free energies were calculated considering various potential metal active sites to reveal the energy barriers of adsorption/desorption of key intermediates. As shown in Fig. 4f, the energy barriers (ΔG) for each step among various active sites were quite different. For the Fe/Co/Ni sites in the FeCoNiPdWOOH model, the third step (formation of $^*\text{OOH}$ from $^*\text{O}$ with OH^- in the electrolyte) exhibited the largest barrier. On the other hand, for Pd and W sites, the ΔG values slightly increased at the second step and first step, respectively. Accordingly, Fe/Co/Ni active sites exhibited lower overpotentials than those of Pd and W sites, respectively, under the equilibrium potential (1.23 eV, Fig. S28, ESI†). Thus, in FeCoNiPdWOOH, activity was associated with Fe/Co/Ni active sites, and the third reaction step was the rate-determining step (RDS) during the four-electron transfer process. To visualize the electronic environment during the reaction coordinates of OER, the PDOS of the most stable binding of key intermediates ($^*\text{OH}$, $^*\text{O}$, $^*\text{OOH}$, and $^*\text{O}_2$) is plotted in Fig. 4g. The σ components of O-2p orbitals facilitated the electron transfer of sequential adsorbed intermediates. From the initial OH species to the final product O_2 , the consecutive upshifting of the σ orbitals demonstrates efficient electron transfer with low barriers for intermediate transformation, which is consistent with the highly efficient OER reaction trend.

Notably, all of the Fe, Co, and Ni sites on the FeCoNiPdWOOH model showed smaller energy barriers than within the other models, demonstrating the significant effect of all the

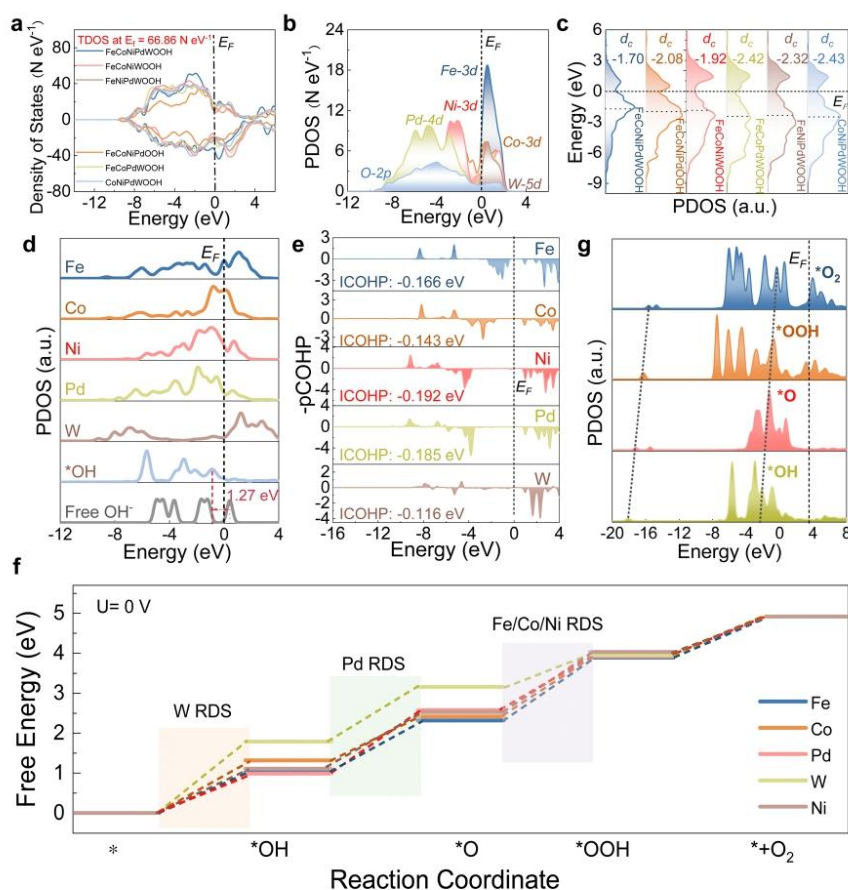


Fig. 4 DFT calculation results. (a) TDOS of FeCoNiPdWOOH, FeCoNiPdOOH, FeCoNiWOOH, FeCoPdWOOH, FeNiPdWOOH, and CoNiPdWOOH. (b) PDOS of FeCoNiPdWOOH. (c) Electronic density of states of the d-band for the metal atoms in various models. (d) PDOS for OH adsorption at various active sites. (e) COHP bonding analysis of M–O interactions (M in the surface site over FeCoNiPdWOOH and O in adsorbed OH). (f) Standard free energy diagram of the OER process at 0 V of FeCoNiPdWOOH for various active sites. (g) PDOS of key intermediates over Ni sites in FeCoNiPdWOOH.

elements in the reconstructed sample (Fig. S29, ESI[†]). Consequently, Fe/Co/Ni are identified as the main active sites for OER, which is consistent with the experimental results. In particular, the strong and positive effect of Pd was further demonstrated by DFT calculations over FeCoNiPdWOOH and Pd-free FeCoNiWOOH models. Pd benefits the electron transfer (Fig. S30 and S31, ESI[†]), optimization of adsorption configuration (Fig. S32, ESI[†]), and electron interaction between the oxygen intermediates (Fig. S33, ESI[†]). Overall, the synergistic effect of the multiple metal atoms, materialized through an efficient p-d orbital coupling and moderate d-band center, optimized the adsorption/desorption of OER intermediates to promote OER kinetics.

In summary, the FeCoNiPdWOOH reconstructed from FeCoNiPdW HEP is highly active towards OER. In the reconstructed

phase, Ni and Pd are favorable for the initial hydroxide adsorption, facilitating the subsequent electron transfer reaction steps. Subsequently, Fe/Co/Ni as the main active sites having favorable OER reaction intermediate adsorption energies, due to their electronic modification by Pd and W. Furthermore, XAS revealed unusually high oxidation states of Fe (+3.1), Co (+3.3), and Ni (+3.8) during the OER, which is crucial to promote the OER reaction.^{90–94}

2.4 ORR

2.4.1 ORR catalytic performance. HEPs were further evaluated towards the ORR in 0.1 M KOH using a rotating ring-disk electrode (RRDE). A large cathodic peak is observed when the electrolyte is saturated with O₂ compared with Ar, indicating a

notable ORR electrochemical activity for the FeCoNiPdWP (Fig. 5a). Fig. 5b and Fig. S34 and S35 (ESI[†]) show the LSV curves with various rotation speeds in the range 400–2500 rpm for the different metal phosphides and a commercial Pd/C reference catalyst. As shown in Fig. 5c, the limiting diffusion current density for the metal phosphides complies with the trend of FeCoNiPdWP (5.37 mA cm^{-2}) > CoNiPdWP (4.37 mA cm^{-2}) > FeCoPdWP (2.77 mA cm^{-2}) > FeCoNiPdP (2.08 mA cm^{-2}) > FeNiPdWP (1.67 mA cm^{-2}). The half-wave potentials, extracted from the LSV curves at 1600 rpm, of the different metal phosphides follow the same trend as the limiting diffusion current density, with FeCoNiPdWP showing the highest value at 0.81 V. This value is very close to that obtained for Pd/C, at 0.82 V. When LSV curves are normalized to the quantity of Pd, FeCoNiPdWP and commercial Pd/C catalysts show similar half-wave potentials but FeCoNiPdWP is characterized by a significantly higher current density (Fig. S36, ESI[†]). Overall, FeCoNiPdWP exhibits excellent ORR activity, matching that of Pd/C and state-of-the-art ORR catalysts, as shown in Fig. 5d and Table S5 (ESI[†]).^{14,52,54,56,78,102–113} Besides, FeCoNiPdWP displays superior ORR stability with just a slight performance degradation after 5000 cycles (Fig. 5e), implying much more stable cycling performance than the quaternary metal phosphides (Fig. S37, ESI[†]).

2.4.2 HEP reconstruction during ORR. After the ORR stability test, the XRD main peak of HEPs is still visible, but it exhibits a broader half-width, indicating a loss of crystallinity or a reduction of the size of the HEP crystal domains during the ORR (Fig. S38, ESI[†]). High-resolution XPS spectra of FeCoNiPdWP HEPs after long-term ORR are displayed in Fig. S39 (ESI[†]). The W 5d and Pd 5d XPS spectra display a unique

contribution assigned to W–P and Pd–P chemical environments. On the other hand, the Fe 3d, Co 3d, and Ni 3d spectra display two coordination environments, M–P and M–O(H). Besides, as shown in Fig. S40 (ESI[†]), the O 1s XPS spectrum displays two peaks, which are indexed to O–P bond and O_{OH} and the P 2p XPS spectrum shows two coordination environments, P–O and P–M. Besides, XPS spectra also show that during the ORR, the Fe, Co, and Ni metal ratios at the FeCoNiPdWP surface slightly increase (Fig. S41, ESI[†]). Additionally, the amount of P at the surface significantly decreases, from 16.5% to 11.0%, while that of oxygen increases, from 15.1% to 27.2%. EDS analysis confirms that the overall P content decreases after ORR, while that of O increases, and the overall content of the different metals remains mostly unchanged (Fig. S42, ESI[†]). Thus, a slight enrichment of the surface with the 3d elements, Fe, Co, and Ni, is inferred, which is again related to the higher affinity of these elements for oxygen and OH[−] groups. Nevertheless, this enrichment is less abrupt than that obtained in the more oxidizing OER conditions. Besides, the lower applied voltages also result in a less oxidized HEP surface where Pd and W maintain the phosphide chemical environment. Within its experimental error, EDS elemental maps show that all the metals, P and O are homogeneously distributed at the particle level after the ORR reaction (Fig. S43, ESI[†]). However, AC-HRTEM single particle analyses reveal highly crystalline HEP cores surrounded by about 2 nm amorphous shells. The crystalline cores with a lattice distance of 2.39 Å match the (211) crystal plane of the rhombohedral Pd₁₅P₂ phase, corresponding to the main XRD peak at $2\theta = 39^\circ$ (Fig. S44, ESI[†]). According to XPS data, the amorphous shells are enriched with Fe, Co, and Ni in a hydroxide or

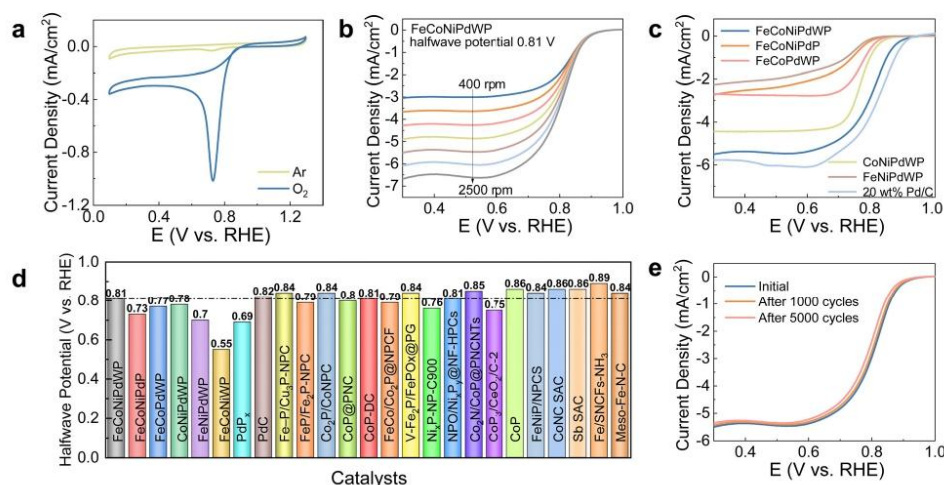


Fig. 5 ORR performance. (a) CV curves measured in Ar and O₂ saturated electrolytes of FeCoNiPdWP. (b) LSV curves of FeCoNiPdWP at different rotation speeds in the range 400–2500 rpm. (c) LSV curves at 1600 rpm for different metal phosphides and Pd/C catalysts. (d) Half-wave potential comparison between metal phosphides and Pd/C catalysts prepared in this work and recently reported state-of-the-art ORR catalysts. (e) Stability of FeCoNiPdWP HEPs during 5000 cycles.

oxyhydroxide chemical environment while also containing notable concentrations of W-P and Pd-P. The higher oxidation resistance of W-P and Pd-P during the ORR process is attributed to their stronger bond with shorter bond lengths, as calculated by DFT (Fig. S45, ESI†). Additionally, W and Pd exhibit greater stability due to more negative standard enthalpies^{114–116} and possess much larger standard redox electrode potentials compared to Fe, Co, and Ni.

2.4.3 HEP element roles in ORR. Electrochemical measurements were first used to investigate the different element roles in FeCoNiPdWP HEP for ORR. Without Pd, FeCoNiWP displays a very weak catalytic ability (Fig. S46a and b, ESI†), demonstrating the key role played by Pd as an active ORR site. Besides, the half-wave potential of PdP_x is also relatively low, at 0.69 V (Fig. S47a and b, ESI†). Thus, while Pd serves as the active site, it doesn't exhibit high catalytic ability within a PdP_x environment. This reinforces the importance of other metals—Fe, Co, Ni, and W—in enhancing and stimulating the catalytic ability of Pd sites within the phosphide environment.

An ORR electron transfer number (n) over 3.9 is obtained for FeCoNiPdWP, CoNiPdWP, FeCoPdWP, PdP_x, and Pd/C, implying a 4 electron pathway (Fig. S46c, S47c and S48a, ESI†) at 0.5 V vs. RHE, where a stable limiting diffusion current density is measured. In contrast, FeCoNiPdP, FeNiPdWP, and FeCoNiWP are characterized by smaller n values, in the range 3.6–3.8, indicating the coexistence of the 4 electron and 2 electron pathways. The hydrogen peroxide (H₂O₂) yields further confirm the pathway assignment (Fig. S46d, S47d and S48b, ESI†). These results point at Pd, Co, and W as collectively assuming a more fundamental role in fine-tuning the reaction pathway, thereby amplifying the ORR performance of FeCoNiPdWP HEPs compared with the quaternary metal phosphides.

DFT calculations were further used to gain an understanding of the catalytic mechanism and element roles in the reconstructed HEPs during ORR. The reconstructed HEP model was built considering the experimental results, *i.e.* a HEP core with a ~2 nm shell rich in Fe, Co, and Ni in a hydroxide environment and Pd and W in a phosphide environment. We denote this reconstructed HEP as FeCoNiPdWPOH (Fig. S49, ESI†). In the PDOS spectra, the good overlap between different metal elements-d orbitals and with the O-p orbitals implies possible p-p/p-d/d-d orbital coupling, which might further promote electron transfer efficiency (Fig. S50, ESI†).

The site-dependent PDOS of individual metal components located within or at the surface of the FeCoNiPdWPOH was also taken into consideration to appreciate their roles in the enhancement of ORR activity (Fig. 6a). From the reconstructed FeCoNiPdWPOH interior to the surface, the e_g - t_{2g} splitting of Fe-3d orbitals gradually decreased. The alleviated e_g - t_{2g} splitting could lead to higher valence states over the surface but also reduce the energy barrier of electron transfer from the electrocatalysts to the adsorbates to improve the ORR performance. Co sites displayed a site-independent electronic structure from the interior to the surface, which could endow the stable adsorption of intermediates and initial electroactive features during the ORR (Fig. 6b). On the other hand, the Ni-3d and Pd-4d bands

gradually approach the E_F from FeCoNiPdWPOH interior to the surface, suggesting improved electroactivity of the surface metal sites (Fig. 6c and d). In contrast, the W-5d orbitals demonstrated an upshifting trend away from E_F , leading to decreasing valence states (Fig. 6e). This compensation of the PDOS trend, facilitated by the W-5d orbitals, contributes to the high electroactivity of the Pd/Ni/Co/Fe surface sites.

The ORR Gibbs energy barrier at various metal sites in FeCoNiPdWPOH was also calculated. As shown in Fig. 6f and Fig. S51 (ESI†), notably, among all of the various metal sites, Pd sites displayed the smallest energy barrier with just a 0.20 eV of the RDS for the conversion from *OOH to O*. Thus, Pd sites show the most thermodynamically favorable process, which is consistent with the experimental results. In addition, the PDOS of key ORR intermediates displayed a gradual downshifting of the O-p orbitals, indicating the reduction trends and highly efficient intermediate conversions for FeCoNiPdWPOH (Fig. 6g).

O₂ adsorption results in strong local charge redistribution over the Pd active sites, causing electron migration from the surface to the adsorbed *O₂ species (Fig. S52, ESI†). The PDOS for adsorbed O₂ is down-shifted compared with that of the free O₂ (Fig. S53, ESI†), further revealing the strong interaction between the Pd sites and O₂. Besides, the final product H₂O could easily escape from the surface of FeCoNiPdWPOH (Fig. S54, ESI†). The adsorption and desorption ability of the oxygen intermediates for Pd sites can be modulated by the introduction of other metals, as determined by the optimum d_e values (Fig. S55, ESI†).

Overall, FeCoNiPdWP shows excellent ORR performance with large limiting current density, high half-wave potentials, four electron-transfer pathways, and long-term cycling performance. In FeCoNiPdWP, Pd was found to be the most active element among the five metals within the reconstructed FeCoNiPdWPOH leading to the excellent ORR catalytic performance. The strong d-d orbital coupling of different elements, especially Pd, Co, and W, fine-tunes ORR electron transfer pathways and the surface electron modulation of Pd with other metal elements decreases the energy barrier during the ORR.

2.5 HEP as bifunctional oxygen catalysts

A key performance parameter to evaluate the oxygen bifunctional catalytic performance is the potential gap (E_{gap}) between the OER overpotential at 10 mA cm⁻² ($E_j = 10$) and the ORR half-wave potential ($E_{1/2}$). A smaller E_{gap} value implies a better bifunctional performance, thus enabling ZABs with higher charge/discharge energy efficiency. Due to the excellent OER and ORR performance, the reconstructed FeCoNiPdWP shows an extremely low E_{gap} value of 0.65 V in 0.1 M KOH, much lower than the combination of the benchmark OER and ORR catalysts, Pd/C and RuO₂, resulting in an E_{gap} of 0.75 V (Fig. 7a). Besides, the FeCoNiPdWP exhibits an outstanding low bifunctional E_{gap} compared with state-of-the-art bifunctional oxygen catalysts, as shown in Fig. 7b and Table S6 (ESI†).^{4,52,54,56,78,108,109,111,112,117–121} The remarkable dual functionality of the reconstructed FeCoNiPdWP in both OER and ORR can be attributed to the distinct contributions and cooperative interactions of each metal involved. While OER and ORR typically

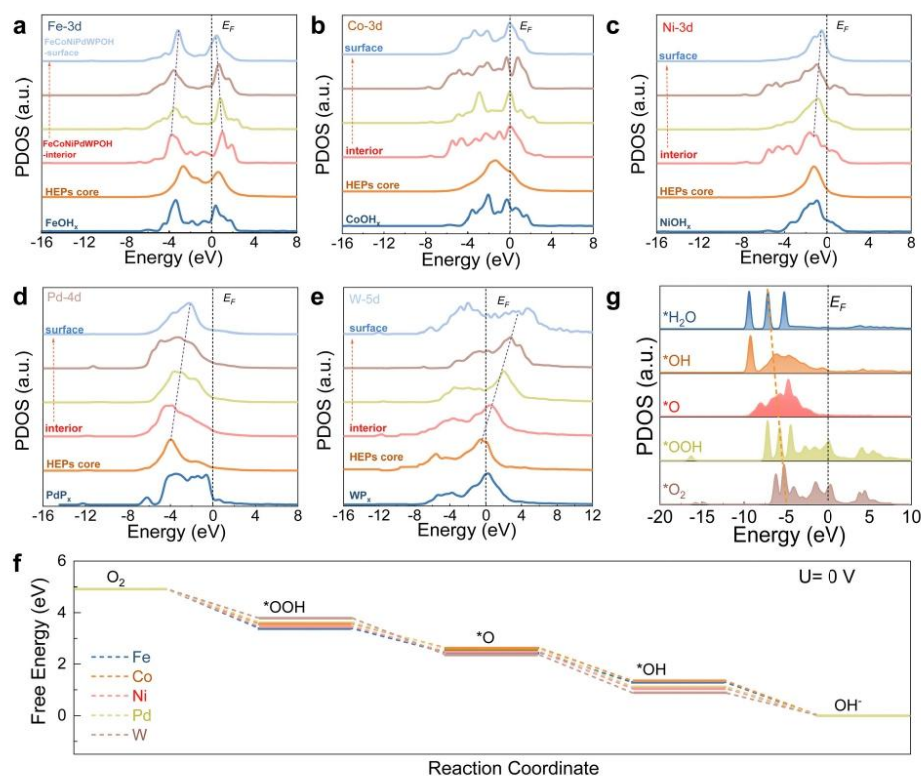


Fig. 6 DFT calculations for ORR. (a)–(e) Site-dependent PDOSs of Fe, Co, Ni, Pd, and W sites in the FeCoNiPdWPOH structure. (f) Standard free energy diagram of the ORR process at 0 V of various active sites on the surface-reconstructed samples. (g) PDOS of key intermediates over Pd sites in FeCoNiPdWPOH.

necessitate varying strengths in binding with the oxygen intermediates, the distinctive roles played by each element within the reconstructed FeCoNiPdWP transcend these conventional constraints. In the OER process, Fe, Co, and Ni emerge as the primary active sites, whereas in ORR, Pd takes on the leading role, complemented by the involvement of Co and W in modulating the electron transfer pathway. The different metal elements play distinctive roles in OER and ORR, respectively, and their synergistic interaction maximizes the performance of the resulting HEM.

2.6 ZAB performance

FeCoNiPdWP was then used as the oxygen cathode in aqueous rechargeable ZABs. Reference ZABs were also assembled with a combination of 20 wt% Pt/C and RuO₂ (Pt/C&RuO₂) as the cathode. Fig. 7c shows a schematic of the ZAB architecture. As shown in Fig. 7d, the ZAB with the FeCoNiPdWP-based air cathode exhibits an open-circuit potential (OCP) of 1.60 V, which is 96.4% of the theoretical limit (1.66 V) and higher than that of the reference Pt/C&RuO₂-based ZAB at 1.56 V. The high OCP values could light a red-screen LED, proving its potential for practical application. The

peak power density of the FeCoNiPdWP HEPs-based ZAB is 123 mW cm⁻², significantly above that of the Pt/C&RuO₂-based ZAB at 111 mW cm⁻² (Fig. 7e). The specific capacity and energy density of the FeCoNiPdWP-based ZAB are 886 mA h g_{Zn}⁻¹ and 1063.2 mW h g_{Zn}⁻¹ at a current density of 8 mA cm⁻², higher than those of the Pt/C&RuO₂-based ZAB at 793 mA h g_{Zn}⁻¹ and 911.9 mW h g_{Zn}⁻¹ (Fig. 7f). The higher specific capacity and energy density are directly attributed to the improved ORR performance of the FeCoNiPdWP-based air cathode, which is the primary factor limiting the discharge process. The FeCoNiPdWP-based ZAB not only excels in performance compared with the reference ZAB tested here but also stands out when compared with state-of-the-art ZABs (Table S7, ESI†).

The rate performance of the FeCoNiPdWP-based ZAB was further evaluated. As shown in Fig. S56 and S57 (ESI†), the FeCoNiPdWP-based ZAB exhibits stable charge-discharge curves at the current density of 2–18 mA cm⁻², with an energy efficiency in the range of 70–50%.

The long-term stability of the ZABs was also measured with continuous charge/discharge cycles at a current density

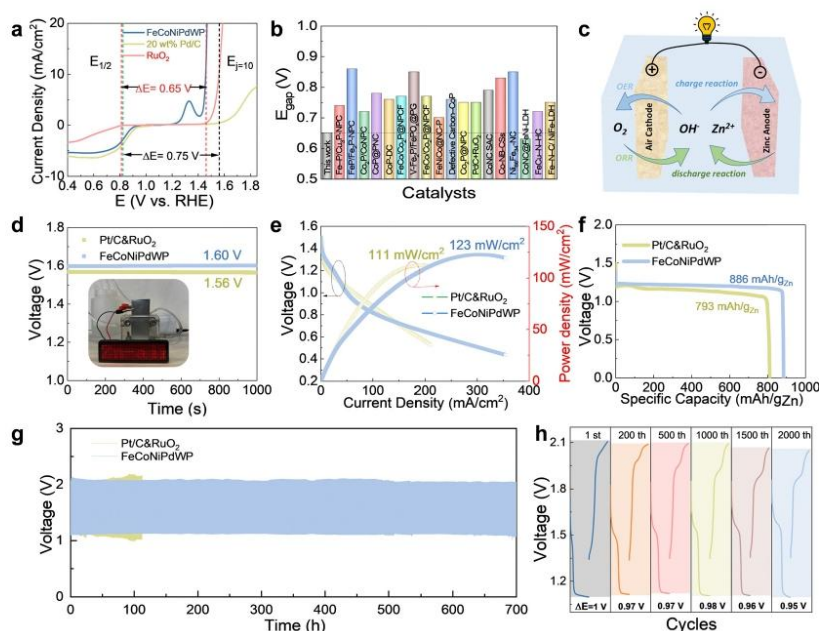


Fig. 7 Oxygen bifunctional properties and ZAB performance. (a) ORR/OER bifunctional LSV curves of different electrodes. (b) Comparison of the E_{gap} values of FeCoNiPdWP and other state-of-the-art bifunctional oxygen catalysts. (c) ZAB schematic diagram. (d) OCP measurements, (e) power density plots, and (f) specific capacity comparisons between a FeCoNiPdWP- and a Pt/C@RuO₂-based ZAB. Photograph of a red LED screen powered by a FeCoNiPdWP-based ZAB is also shown in (d). (g) Galvanostatic discharge–charge curves with 10 min discharge and 10 min charge cycles at a current density of 8 mA cm^{−2} of FeCoNiPdWP- and Pt/C@RuO₂-based ZABs. (h) Enlarged galvanostatic discharge–charge cycles at the specific cycles (1st, 200th, 500th, 1000th, 1500th, and 2000th) for 20 min of the FeCoNiPdWP-based ZAB.

of 8 mA cm^{−2}. As shown in Fig. 7g, the FeCoNiPdW-based ZAB can be stable over 700 h, *i.e.* 1 month, of continuous cycling (over 2000 cycles). In contrast, the Pt/C@RuO₂-based ZAB is stable for just about 100 h, *i.e.* 300 cycles. Fig. 7h shows the enlarged galvanostatic discharge–charge cycles of FeCoNiPdWP HEPs-based ZABs at the specific cycles at 1st, 200th, 500th, 1000th, and 2000th cycles. The initial charging/discharging potential gap is 1.0 V. With continuous cycling, the potential gap is decreased to 0.97 V at 200 cycles, and it remains in the range of 0.95–0.96 V after 1000–2000 cycles, further proving its good stability.

3. Conclusion

FeCoNiPdWP HEP nanoparticles were synthesized using a mild colloidal method and tested as bifunctional OER/ORR catalysts. These HEPs demonstrated exceptional OER performance, with a low overpotential of 227 mV at 10 mA cm^{−2} and a Tafel slope of 33 mV dec^{−1}. The outstanding OER performance is attributed to a reconstructed FeCoNiPdWOOH surface rich in high-oxidation-state Fe, Co, and Ni (Fe = 3.1; Co = 3.3; Ni = 3.8) as main active sites, Pd aiding in OH[−] adsorption, and W optimizing oxygen

intermediate adsorption *via* electronic structure modulation. For ORR, FeCoNiPdWP HEPs show a half-wave potential of 0.81 V and efficient four-electron transfer pathways. During ORR, the surface of the HEP was also slightly enriched in Fe, Co, and Ni and reconstructed into a FeCoNiPdWPOH, with Fe/Co/Ni found as oxyhydroxides but with Pd and W maintaining the phosphide chemical environment as observed by XPS analysis. This unique FeCoNiPdWPOH surface, together with the active role of Pd and the influence of Co and W in modulating the electron transfer pathways, significantly enhances the ORR performance. Overall, each element within FeCoNiPdWP HEPs plays a crucial role in enhancing both OER and ORR performances. The combination of all these elements playing distinctive roles and the switchable active sites in redox reactions transcends the usual constraints of bifunctional catalysts, which generally excel in only one of these reactions. As a result, FeCoNiPdWP shows an extremely low E_{gap} value of 0.65 V and FeCoNiPdWP-based ZABs exhibit outstanding performance and stability for over 700 h. This work provides a platform to understand the different surface reconstruction behaviors of HEP catalysts and the distinct element roles in OER and ORR reactions, which paves the way for designing advanced bifunctional oxygen catalysis, potentially based on HEMs.

Author contributions

Ren He (data curation: lead; formal analysis: lead; investigation: lead; methodology: lead; resources: lead; validation: lead; visualization: lead; writing – original draft: lead). Shiqi Wang (data curation: equal; software: lead; visualization: equal; writing – original draft: equal). Linlin Yang (data curation: equal; formal analysis: equal; validation: equal; writing – original draft: lead). Sharona Horta (formal analysis: equal; investigation: equal; resources: equal). Yang Ding (formal analysis: supporting; investigation: supporting). Chong Di (data curation: supporting; visualization: supporting). Xuesong Zhang (data curation: supporting; formal analysis: supporting). Ying Xu (data curation: supporting; resources: supporting). Maria Ibáñez (formal analysis: supporting; resources: supporting). Yingtang Zhou (formal analysis: supporting; validation: supporting). Stefan Mebs (formal analysis: supporting; investigation: supporting). Holger Dau (formal analysis: supporting; visualization: supporting). Jan Niklas Hausmann (data curation: equal; formal analysis: equal; writing – original draft: equal). Wenyi Huo (formal analysis: equal; software: lead; writing – original draft: equal; writing – review & editing: equal; supervision: equal). Prashanth W. Menezes (data curation: equal; formal analysis: equal; resources: equal; writing – original draft: equal). Andreu Cabot (conceptualization: lead; funding acquisition: lead; project administration: lead; resources: lead; writing – review & editing: lead).

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

- 1 X. Zhu, C. Hu, R. Amal, L. Dai and X. Lu, *Energy Environ. Sci.*, 2020, **13**, 4536–4563.
- 2 J. N. Liu, C. X. Zhao, D. Ren, J. Wang, R. Zhang, S. H. Wang, C. Zhao, B. Q. Li and Q. Zhang, *Adv. Mater.*, 2022, **34**, e2109407.
- 3 W. Niu, Z. Li, K. Marcus, L. Zhou, Y. Li, R. Ye, K. Liang and Y. Yang, *Adv. Energy Mater.*, 2018, **8**, 1701642.
- 4 C. X. Zhao, J. N. Liu, J. Wang, D. Ren, J. Yu, X. Chen, B. Q. Li and Q. Zhang, *Adv. Mater.*, 2021, **33**, e2008606.
- 5 T. Binnering and M. L. Doublet, *Energy Environ. Sci.*, 2022, **15**, 2519–2528.
- 6 J. Chen, M. Aliasgar, F. B. Zamudio, T. Zhang, Y. Zhao, X. Lian, L. Wen, H. Yang, W. Sun, S. M. Kozlov, W. Chen and L. Wang, *Nat. Commun.*, 2023, **14**, 1711.
- 7 M. Liu, Z. Zhao, X. Duan and Y. Huang, *Adv. Mater.*, 2019, **31**, e1802234.
- 8 J. Zhang, J. Lian, Q. Jiang and G. Wang, *Chem. Eng. J.*, 2022, **439**, 135634.
- 9 C. Tang, H. S. Wang, H. F. Wang, Q. Zhang, G. L. Tian, J. Q. Nie and F. Wei, *Adv. Mater.*, 2015, **27**, 4516–4522.
- 10 L. Gui, Z. Wang, K. Zhang, B. He, Y. Liu, W. Zhou, J. Xu, Q. Wang and L. Zhao, *Appl. Catal., B*, 2020, **266**, 118656.
- 11 C. Li, M. Wu and R. Liu, *Appl. Catal., B*, 2019, **244**, 150–158.
- 12 J. Zhang, T. Wang, D. Pohl, B. Rellinghaus, R. Dong, S. Liu, X. Zhuang and X. Feng, *Angew. Chem., Int. Ed.*, 2016, **55**, 6702–6707.
- 13 X. Jia, Y. Zhao, G. Chen, L. Shang, R. Shi, X. Kang, G. I. N. Waterhouse, L. Z. Wu, C. H. Tung and T. Zhang, *Adv. Energy Mater.*, 2016, **6**, 1502585.
- 14 J. Li, Y. Kang, Z. Lei and P. Liu, *Appl. Catal., B*, 2023, **321**, 122029.
- 15 L. Yang, X. Zeng, D. Wang and D. Cao, *Energy Storage Mater.*, 2018, **12**, 277–283.
- 16 B. Q. Li, C. X. Zhao, S. Chen, J. N. Liu, X. Chen, L. Song and Q. Zhang, *Adv. Mater.*, 2019, **31**, e1900592.
- 17 Y. Zhang, H. Jiang, Y. Lin, H. Liu, Q. He, C. Wu, T. Duan and L. Song, *Adv. Mater. Interfaces*, 2018, **5**, 1800392.
- 18 Y. Mei, Y. Feng, C. Zhang, Y. Zhang, Q. Qi and J. Hu, *ACS Catal.*, 2022, **12**, 10808–10817.
- 19 J. Kwon, S. Sun, S. Choi, K. Lee, S. Jo, K. Park, Y. K. Kim, H. B. Park, H. Y. Park, J. H. Jang, H. Han, U. Paik and T. Song, *Adv. Mater.*, 2023, **35**, e2300091.
- 20 H. Zhu, S. Sun, J. Hao, Z. Zhuang, S. Zhang, T. Wang, Q. Kang, S. Lu, X. Wang, F. Lai, T. Liu, G. Gao, M. Du and D. Wang, *Energy Environ. Sci.*, 2023, **16**, 619–628.
- 21 T. A. A. Batchelor, J. K. Pedersen, S. H. Winther, I. E. Castelli, K. W. Jacobsen and J. Rossmeisl, *Joule*, 2019, **3**, 834–845.

- 22 Y. Chida, T. Tomimori, T. Ebata, N. Taguchi, T. Ioroi, K. Hayashi, N. Todoroki and T. Wadayama, *Nat. Commun.*, 2023, **14**, 4492.
- 23 A. Ostovari Moghaddam, A. Cabot and E. A. Trofimov, *Int. J. Refract. Met. Hard Mater.*, 2021, **97**, 105504.
- 24 R. He, L. Yang, Y. Zhang, D. Jiang, S. Lee, S. Horta, Z. Liang, X. Lu, A. O. Moghaddam, J. Li, M. Ibanez, Y. Xu, Y. Zhou and A. Cabot, *Adv. Mater.*, 2023, **35**, e2303719.
- 25 R. He, L. Yang, Y. Zhang, X. Wang, S. Lee, T. Zhang, L. Li, Z. Liang, J. Chen, J. Li, A. Ostovari Moghaddam, J. Llorca, M. Ibáñez, J. Arbiol, Y. Xu and A. Cabot, *Energy Storage Mater.*, 2023, **58**, 287–298.
- 26 L. Yang, R. He, X. Wang, T. Yang, T. Zhang, Y. Zuo, X. Lu, Z. Liang, J. Li, J. Arbiol, P. R. Martínez-Alanis, X. Qi and A. Cabot, *Nano Energy*, 2023, **115**, 108714.
- 27 L. Gao, X. Cui, C. D. Sewell, J. Li and Z. Lin, *Chem. Soc. Rev.*, 2021, **50**, 8428–8469.
- 28 J. Liu, S. Wang, K. Kravchyk, M. Ibáñez, F. Krumeich, R. Widmer, D. Nasiou, M. Meyns, J. Llorca, J. Arbiol, M. V. Kovalenko and A. Cabot, *J. Mater. Chem. A*, 2018, **6**, 10958–10966.
- 29 M. I. Díez-García, G. Montana-Mora, M. Botifoll, A. Cabot, J. Arbiol, M. Qamar and J. R. Morante, *ACS Appl. Energy Mater.*, 2023, **6**, 5690–5699.
- 30 J. Liu, X. Yu, R. Du, C. Zhang, T. Zhang, J. Llorca, J. Arbiol, Y. Wang, M. Meyns and A. Cabot, *Appl. Catal., B*, 2019, **256**, 117846.
- 31 X. Wang, L. Yang, C. Xing, X. Han, R. Du, R. He, P. Guardia, J. Arbiol and A. Cabot, *Nanomaterials*, 2022, **12**, 1098.
- 32 J. Liu, Z. Wang, J. David, J. Llorca, J. Li, X. Yu, A. Shavel, J. Arbiol, M. Meyns and A. Cabot, *J. Mater. Chem. A*, 2018, **6**, 11453–11462.
- 33 N. Khodayar, A. Noori, M. S. Rahmanifar, M. Moloudi, N. Hassani, M. Neek-Amal, M. F. El-Kady, N. B. Mohamed, X. Xia, Y. Zhang, R. B. Kaner and M. F. Mousavi, *Energy Environ. Sci.*, 2024, **17**, 5200–5215.
- 34 D. Lai, Q. Kang, F. Gao and Q. Lu, *J. Mater. Chem. A*, 2021, **9**, 17913–17922.
- 35 Y. Li, Z. Dong and L. Jiao, *Adv. Energy Mater.*, 2019, **10**, 1902104.
- 36 Y. Shi, M. Li, Y. Yu and B. Zhang, *Energy Environ. Sci.*, 2020, **13**, 4564–4582.
- 37 H. Li, C. Zhang, W. Xiang, M. A. Amin, J. Na, S. Wang, J. Yu and Y. Yamauchi, *Chem. Eng. J.*, 2023, **452**, 139104.
- 38 G. Ke, F. Duan, B. Liu, X. Liu, J. Wen, B. Jia, X. Liu, H. He and Y. Zhou, *J. Alloys Compd.*, 2023, **934**, 167883.
- 39 K. Kim, K. Min, Y. Go, Y. Lee, S. E. Shim, D. Lim and S.-H. Baeck, *Appl. Catal., B*, 2022, **315**, 121501.
- 40 Z. Wang, J. Ang, J. Liu, X. Y. D. Ma, J. Kong, Y. Zhang, T. Yan and X. Lu, *Appl. Catal., B*, 2020, **263**, 118344.
- 41 W.-W. Tian, J.-T. Ren and Z.-Y. Yuan, *Appl. Catal., B*, 2022, **317**, 121764.
- 42 Z. Li, M. Chen, L. Zhang, R. Xing, J. Hu, X. Huang, C. Zhou, Y. Zhou, T. Wågberg and G. Hu, *J. Mater. Chem. A*, 2023, **11**, 2155–2167.
- 43 C. He, L. Yang, X. Peng, S. Liu, J. Wang, C. Dong, D. Du, L. Li, L. Bu and X. Huang, *ACS Nano*, 2023, **17**, 5861–5870.
- 44 L. Yang, R. He, M. Botifoll, Y. Zhang, Y. Ding, C. Di, C. He, Y. Xu, L. Balcells, J. Arbiol, Y. Zhou and A. Cabot, *Adv. Mater.*, 2024, **36**, e2400572.
- 45 L. Wu, T. Guo and T. Li, *iScience*, 2021, **24**, 102398.
- 46 H. Xie, S. Chen, J. Liang, T. Wang, Z. Hou, H. L. Wang, G. Chai and Q. Li, *Adv. Funct. Mater.*, 2021, **31**, 2100883.
- 47 F. Lin, F. Lv, Q. Zhang, H. Luo, K. Wang, J. Zhou, W. Zhang, W. Zhang, D. Wang, L. Gu and S. Guo, *Adv. Mater.*, 2022, **34**, e2202084.
- 48 T. Wang, A. Chutia, D. J. L. Brett, P. R. Shearing, G. He, G. Chai and I. P. Parkin, *Energy Environ. Sci.*, 2021, **14**, 2639–2669.
- 49 S. Wang, Y. Xie, K. Shi, W. Zhou, Z. Xing, K. Pan and A. Cabot, *ACS Sustainable Chem. Eng.*, 2020, **8**, 5920–5926.
- 50 J. Liu, Z. Luo, J. Li, X. Yu, J. Llorca, D. Nasiou, J. Arbiol, M. Meyns and A. Cabot, *Appl. Catal., B*, 2019, **242**, 258–266.
- 51 J. Liu, M. Meyns, T. Zhang, J. Arbiol, A. Cabot and A. Shavel, *Chem. Mater.*, 2018, **30**, 1799–1807.
- 52 X. Yang, F. Wang, Z. Jing, M. Chen, B. Wang, L. Wang, G. Qu, Y. Kong and L. Xu, *Small*, 2023, **19**, e2301985.
- 53 Y. Guo, J. Tang, Z. Wang, Y. Sugahara and Y. Yamauchi, *Small*, 2018, **14**, e1802442.
- 54 H. Liu, J. Guan, S. Yang, Y. Yu, R. Shao, Z. Zhang, M. Dou, F. Wang and Q. Xu, *Adv. Mater.*, 2020, **32**, e2003649.
- 55 P. He, X. Y. Yu and X. W. Lou, *Angew. Chem., Int. Ed.*, 2017, **56**, 3897–3900.
- 56 Q. Shi, Q. Liu, Y. Ma, Z. Fang, Z. Liang, G. Shao, B. Tang, W. Yang, L. Qin and X. Fang, *Adv. Energy Mater.*, 2020, **10**, 1903854.
- 57 F. Luo, Q. Zhang, X. Yu, S. Xiao, Y. Ling, H. Hu, L. Guo, Z. Yang, L. Huang, W. Cai and H. Cheng, *Angew. Chem., Int. Ed.*, 2018, **57**, 14862–14867.
- 58 B. Qiu, L. Cai, Y. Wang, Z. Lin, Y. Zuo, M. Wang and Y. Chai, *Adv. Funct. Mater.*, 2018, **28**, 1706008.
- 59 J. Wang and F. Ciucci, *Appl. Catal., B*, 2019, **254**, 292–299.
- 60 C. Wang, W. Chen, D. Yuan, S. Qian, D. Cai, J. Jiang and S. Zhang, *Nano Energy*, 2020, **69**, 104453.
- 61 Y. Deng, Y. Cao, Y. Xia, X. Xi, Y. Wang, W. Jiang, D. Yang, A. Dong and T. Li, *Adv. Energy Mater.*, 2022, **12**, 2202394.
- 62 G. Zhou, M. Li, Y. Li, H. Dong, D. Sun, X. Liu, L. Xu, Z. Tian and Y. Tang, *Adv. Funct. Mater.*, 2019, **30**, 1905252.
- 63 R. Zhang, W. Liu, F.-M. Zhang, Z.-D. Yang, G. Zhang and X. C. Zeng, *Appl. Catal., B*, 2023, **325**, 122366.
- 64 Y. Chen, J. Xu, M. Jiang, L. Wang, R. Ma, Y. Chen, Z. H. Xie, P. Munroe, F. Hu, L. Li and S. Peng, *Adv. Energy Mater.*, 2023, **14**, 2303450.
- 65 Y. Gao, D. Zheng, Q. Li, W. Xiao, T. Ma, Y. Fu, Z. Wu and L. Wang, *Adv. Funct. Mater.*, 2022, **32**, 2203206.
- 66 T. Dai, X. Zhang, M. Sun, B. Huang, N. Zhang, P. Da, R. Yang, Z. He, W. Wang, P. Xi and C. H. Yan, *Adv. Mater.*, 2021, **33**, e2102593.
- 67 S. Pan, H. Li, D. Liu, R. Huang, X. Pan, D. Ren, J. Li, M. Shakouri, Q. Zhang, M. Wang, C. Wei, L. Mai, B. Zhang, Y. Zhao, Z. Wang, M. Graetzel and X. Zhang, *Nat. Commun.*, 2022, **13**, 2294.

- 68 Z. Zhang, X. Li, C. Zhong, N. Zhao, Y. Deng, X. Han and W. Hu, *Angew. Chem., Int. Ed.*, 2020, **59**, 7245–7250.
- 69 J. Wang, S.-J. Kim, J. Liu, Y. Gao, S. Choi, J. Han, H. Shin, S. Jo, J. Kim, F. Ciucci, H. Kim, Q. Li, W. Yang, X. Long, S. Yang, S.-P. Cho, K. H. Chae, M. G. Kim, H. Kim and J. Lim, *Nat. Catal.*, 2021, **4**, 212–222.
- 70 C. Chen, M. Sun, F. Zhang, H. Li, M. Sun, P. Fang, T. Song, W. Chen, J. Dong, B. Rosen, P. Chen, B. Huang and Y. Li, *Energy Environ. Sci.*, 2023, **16**, 1685–1696.
- 71 P. Li, M. Wang, X. Duan, L. Zheng, X. Cheng, Y. Zhang, Y. Kuang, Y. Li, Q. Ma, Z. Feng, W. Liu and X. Sun, *Nat. Commun.*, 2019, **10**, 1711.
- 72 H. Liu, X. Xu, H. Xu, S. Wang, Z. Niu, Q. Jia, L. Yang, R. Cao, L. Zheng and D. Cao, *Appl. Catal., B*, 2021, **297**, 120451.
- 73 L. Tang, L. Yu, C. Ma, Y. Song, Y. Tu, Y. Zhang, X. Bo and D. Deng, *J. Mater. Chem. A*, 2022, **10**, 6242–6250.
- 74 Y. Zhao, Y. Guo, X. F. Lu, D. Luan, X. Gu and X. W. D. Lou, *Adv. Mater.*, 2022, **34**, e2203442.
- 75 S. Zhao, C. Tan, C.-T. He, P. An, F. Xie, S. Jiang, Y. Zhu, K.-H. Wu, B. Zhang, H. Li, J. Zhang, Y. Chen, S. Liu, J. Dong and Z. Tang, *Nat. Energy*, 2020, **5**, 881–890.
- 76 R. Yang, L. An, Y. Zhang, N. Zhang, T. Dai and P. Xi, *ChemCatChem*, 2019, **11**, 6002–6007.
- 77 S. Li, B. Chen, Y. Wang, M. Y. Ye, P. A. van Aken, C. Cheng and A. Thomas, *Nat. Mater.*, 2021, **20**, 1240–1247.
- 78 Y. Li, Y. Liu, Q. Qian, G. Wang and G. Zhang, *Energy Storage Mater.*, 2020, **28**, 27–36.
- 79 A. Dutta, A. K. Samantara, S. K. Dutta, B. K. Jena and N. Pradhan, *ACS Energy Lett.*, 2016, **1**, 169–174.
- 80 L.-A. Stern, L. Feng, F. Song and X. Hu, *Energy Environ. Sci.*, 2015, **8**, 2347–2351.
- 81 Y. Zhao, N. Dongfang, C. A. Triana, C. Huang, R. Erni, W. Wan, J. Li, D. Stoian, L. Pan, P. Zhang, J. Lan, M. Iannuzzi and G. R. Patzke, *Energy Environ. Sci.*, 2022, **15**, 727–739.
- 82 P. Hou, D. Li, N. Yang, J. Wan, C. Zhang, X. Zhang, H. Jiang, Q. Zhang, L. Gu and D. Wang, *Angew. Chem., Int. Ed.*, 2021, **60**, 6926–6931.
- 83 X. Zheng, J. Yang, Z. Xu, Q. Wang, J. Wu, E. Zhang, S. Dou, W. Sun, D. Wang and Y. Li, *Angew. Chem., Int. Ed.*, 2022, **61**, e202205946.
- 84 W. Li, Y. Li, H. Fu, G. Yang, Q. Zhang, S. Chen and F. Peng, *Chem. Eng. J.*, 2020, **381**, 122683.
- 85 J. Duan, S. Chen, A. Vasileff and S. Z. Qiao, *ACS Nano*, 2016, **10**, 8738–8745.
- 86 G. Zhang, G. Wang, Y. Liu, H. Liu, J. Qu and J. Li, *J. Am. Chem. Soc.*, 2016, **138**, 14686–14693.
- 87 B. S. Yeo and A. T. Bell, *J. Phys. Chem. C*, 2012, **116**, 8394–8400.
- 88 D. L. A. de Faria, S. Venâncio Silva and M. T. de Oliveira, *J. Raman Spectrosc.*, 1997, **28**, 873–878.
- 89 R. Beltrán-Suito, P. W. Menezes and M. Driess, *J. Mater. Chem. A*, 2019, **7**, 15749–15756.
- 90 H. N. Nong, L. J. Falling, A. Bergmann, M. Klingenhof, H. P. Tran, C. Spori, R. Mom, J. Timoshenko, G. Zichittella, A. Knop-Gericke, S. Piccinin, J. Perez-Ramirez, B. R. Cuenya, R. Schlogl, P. Strasser, D. Teschner and T. E. Jones, *Nature*, 2020, **587**, 408–413.
- 91 L. Reith, J. N. Hausmann, S. Mebs, I. Mondal, H. Dau, M. Driess and P. W. Menezes, *Adv. Energy Mater.*, 2023, **13**, 2203886.
- 92 M. Gorlin, J. Ferreira de Araujo, H. Schmies, D. Bernsmeier, S. Drespe, M. Gliech, Z. Jusys, P. Chernev, R. Kraehnert, H. Dau and P. Strasser, *J. Am. Chem. Soc.*, 2017, **139**, 2070–2082.
- 93 J. N. Hausmann, S. Mebs, K. Laun, I. Zebger, H. Dau, P. W. Menezes and M. Driess, *Energy Environ. Sci.*, 2020, **13**, 3607–3619.
- 94 F. Dionigi, Z. Zeng, I. Sinev, T. Merzdorf, S. Deshpande, M. B. Lopez, S. Kunze, I. Zegkinoglou, H. Sarodnik, D. Fan, A. Bergmann, J. Drnc, J. F. Araujo, M. Gliech, D. Teschner, J. Zhu, W. X. Li, J. Greeley, B. R. Cuenya and P. Strasser, *Nat. Commun.*, 2020, **11**, 2522.
- 95 J. N. Hausmann, R. A. Khalaniya, C. Das, I. Remy-Speckmann, S. Berendts, A. V. Shevelkov, M. Driess and P. W. Menezes, *Chem. Commun.*, 2021, **57**, 2184–2187.
- 96 R. D. L. Smith, C. Pasquini, S. Loos, P. Chernev, K. Klingan, P. Kubella, M. R. Mohammadi, D. Gonzalez-Flores and H. Dau, *Nat. Commun.*, 2017, **8**, 2022.
- 97 R. D. L. Smith, C. Pasquini, S. Loos, P. Chernev, K. Klingan, P. Kubella, M. R. Mohammadi, D. González-Flores and H. Dau, *Energy Environ. Sci.*, 2018, **11**, 2476–2485.
- 98 M. Risch, K. Klingan, J. Heidkamp, D. Ehrenberg, P. Chernev, I. Zaharieva and H. Dau, *Chem. Commun.*, 2011, **47**, 11912–11914.
- 99 H. Li, M. Sun, Y. Pan, J. Xiong, H. Du, Y. Yu, S. Feng, Z. Li, J. Lai, B. Huang and L. Wang, *Appl. Catal., B*, 2022, **312**, 121431.
- 100 J. Li, L. Zheng, B. Huang, Y. Hu, L. An, Y. Yao, M. Lu, J. Jin, N. Zhang and P. J. S. Xi, *Small*, 2022, **18**, 2204723.
- 101 B. Bao, Y. Liu, M. Sun, B. Huang, Y. Hu, P. Da, D. Ji, P. Xi and C. H. J. S. Yan, *Small*, 2022, **18**, 2201131.
- 102 R. He, T. Lu, N. Xu, G. Liu, Y. Zhang and J. Qiao, *Chem. Eng. J.*, 2023, **461**, 141843.
- 103 C. Yao, J. Li, Z. Zhang, C. Gou, Z. Zhang, G. Pan and J. Zhang, *Small*, 2022, **18**, e2108094.
- 104 H. Li, Q. Li, P. Wen, T. B. Williams, S. Adhikari, C. Dun, C. Lu, D. Itanze, L. Jiang, D. L. Carroll, G. L. Donati, P. M. Lundin, Y. Qiu and S. M. Geyer, *Adv. Mater.*, 2018, **30**, 1705796.
- 105 J.-T. Ren, Y.-S. Wang, L. Chen, L.-J. Gao, W.-W. Tian and Z.-Y. Yuan, *Chem. Eng. J.*, 2020, **389**, 124408.
- 106 T. Wang, X. Cao, H. Qin, L. Shang, S. Zheng, F. Fang and L. Jiao, *Angew. Chem., Int. Ed.*, 2021, **60**, 21237–21241.
- 107 Y. Wang, J. Liu, T. Lu, R. He, N. Xu and J. Qiao, *Appl. Catal., B*, 2023, **321**, 122674.
- 108 Q. P. Ngo, T. T. Nguyen, M. Singh, R. Balaji, N. H. Kim and J. H. Lee, *Appl. Catal., B*, 2023, **331**, 122674.
- 109 D. Ren, J. Ying, M. Xiao, Y. P. Deng, J. Ou, J. Zhu, G. Liu, Y. Pei, S. Li, A. M. Jauhar, H. Jin, S. Wang, D. Su, A. Yu and Z. Chen, *Adv. Funct. Mater.*, 2019, **30**, 1908167.

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- 110 L. Yang, X. Zhang, L. Yu, J. Hou, Z. Zhou and R. Lv, *Adv. Mater.*, 2022, **34**, e2105410.
- 111 Y. Lin, L. Yang, Y. Zhang, H. Jiang, Z. Xiao, C. Wu, G. Zhang, J. Jiang and L. Song, *Adv. Energy Mater.*, 2018, **8**, 1703623.
- 112 C.-X. Zhao, J.-N. Liu, J. Wang, C. Wang, X. Guo, X.-Y. Li, X. Chen, L. Song, B.-Q. Li and Q. Zhang, *Sci. Adv.*, 2022, **8**, eabn5091.
- 113 Y. Zhou, Y. Yu, D. Ma, A. C. Foucher, L. Xiong, J. Zhang, E. A. Stach, Q. Yue and Y. Kang, *ACS Catal.*, 2020, **11**, 74–81.
- 114 Z. You and I.-H. Jung, *Metall. Mater. Trans. B*, 2020, **51**, 3108–3129.
- 115 R. Ganesan, A. T. Dinsdale and H. Ipser, *Intermetallics*, 2011, **19**, 927–933.
- 116 S. Boone and O. J. Kleppa, *J. Chem. Thermodyn.*, 1991, **23**, 1147–1151.
- 117 Q. Shi, Q. Liu, Y. Zheng, Y. Dong, L. Wang, H. Liu and W. Yang, *Energy Environ. Mater.*, 2021, **5**, 515–523.
- 118 Y. Guo, P. Yuan, J. Zhang, Y. Hu, I. S. Amiinu, X. Wang, J. Zhou, H. Xia, Z. Song, Q. Xu and S. Mu, *ACS Nano*, 2018, **12**, 1894–1901.
- 119 M. Ma, A. Kumar, D. Wang, Y. Wang, Y. Jia, Y. Zhang, G. Zhang, Z. Yan and X. Sun, *Appl. Catal., B*, 2020, **274**, 119091.
- 120 H. Sun, M. Wang, S. Zhang, S. Liu, X. Shen, T. Qian, X. Niu, J. Xiong and C. Yan, *Adv. Funct. Mater.*, 2020, **31**, 2006533.
- 121 S. Drespe, F. Luo, R. Schmack, S. Köhl, M. Gliech and P. Strasser, *Energy Environ. Sci.*, 2016, **9**, 2020–2024.
- 122 E. Vijayakumar, S. Ramakrishnan, C. Sathiskumar, D. J. Yoo, J. Balamurugan, H. S. Noh, D. Kwon, Y. H. Kim and H. Lee, *Chem. Eng. J.*, 2022, **428**, 13115.
- 123 J. Chen, C. Fan, X. Hu, C. Wang, Z. Huang, G. Fu, J. M. Lee and Y. Tang, *Small*, 2019, **15**, e1901518.
- 124 P. Yu, L. Wang, F. Sun, Y. Xie, X. Liu, J. Ma, X. Wang, C. Tian, J. Li and H. Fu, *Adv. Mater.*, 2019, **31**, e1901666.
- 125 P. Peng, L. Shi, F. Huo, C. Mi, X. Wu, S. Zhang and Z. Xiang, *Sci. Adv.*, 2019, **5**, eaaw2322.
- 126 J. Han, H. Bao, J.-Q. Wang, L. Zheng, S. Sun, Z. L. Wang and C. Sun, *Appl. Catal., B*, 2021, **280**, 1194.
- 127 J. Han, X. Meng, L. Lu, J. Bian, Z. Li and C. Sun, *Adv. Funct. Mater.*, 2019, **29**, 1828872.
- 128 M. Moloudi, A. Noori, M. S. Rahmanifar, Y. Shabangoli, M. F. El-Kady, N. B. Mohamed, R. B. Kaner and M. F. Mousavi, *Adv. Energy Mater.*, 2022, **13**, 2203002.
- 129 Z. Wang, J. Ang, B. Zhang, Y. Zhang, X. Y. D. Ma, T. Yan, J. Liu, B. Che, Y. Huang and X. Lu, *Appl. Catal., B*, 2019, **254**, 26–36.
- 130 Z. Pan, H. Chen, J. Yang, Y. Ma, Q. Zhang, Z. Kou, X. Ding, Y. Pang, L. Zhang, Q. Gu, C. Yan and J. Wang, *Adv. Sci.*, 2019, **6**, 1900628.
- 131 J. Qian, X. Guo, T. Wang, P. Liu, H. Zhang and D. Gao, *Appl. Catal., B*, 2019, **250**, 71–77.
- 132 X. Zhao, X. Li, Z. Bi, Y. Wang, H. Zhang, X. Zhou, Q. Wang, Y. Zhou, H. Wang and G. Hu, *J. Energy Chem.*, 2022, **66**, 514–524.